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Aspects of phase equilibria in Fe/Co/2.5 to 3.0 % V alloys

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Remendur alloys, one of which is used as the base material in remanent reed sealed contacts for the communications industry, are ternary alloys containing approximately equal iron and cobalt with 2 to 4 wt % vanadium. The available equilibrium diagram for this system does not provide precise positioning of the phase boundaries in the regions of commercial interest and, consequently, does not permit accurate determination of the amounts of the phases present or their compositions.

This paper reports on the precise determination of five tie lines in the $\alpha_1 + \gamma$ two-phase field in the region of interest, by metallographic and microprobe techniques. In the 900 to 950°C range, this field was found to be narrower than expected from published data. Submicron fcc (γ) particles form during annealing at 600°C by decomposition of a non-equilibrium bcc (α_2) phase into a secondary ordered bcc phase (α_1') and stabilized γ. Deformation, by drawing and by stamping, enhances coercivity in these alloys by promoting a more uniform, more finely divided dispersion of γ particles. Annealed microstructures are especially sensitive to vanadium content, annealing temperature, and annealing time.

1. Introduction

The effects of processing variations on the microstructures of 2.5 to 3.0 wt % V-balance equal Fe/Co alloys, known commercially as Remendur, have been detailed recently [1]. Prior to this, an incomplete understanding of the pertinent phase transformations had led to difficulties in the commercial processing of these alloys into rod and wire. Although earlier work had shown that this alloy could be fabricated under specific conditions [2], no range or limiting conditions for processing were defined.

The initial stages in commercial production of wire, which is used as the base material in remanent reed sealed contacts for the communications industry, consists of hot rolling an ingot into 6.35 mm (0.25 in.) rod at 1100 to 1200°C and cooling in air to room temperature. The rod is reheated to 900 to 950°C for $\frac{1}{2}$ h and quenched into iced brine. Hot ductility is dependent upon the hot working temperature, and cold ductility is dependent upon subsequent annealing temperature, annealing time, and mode of cooling [1, 3]. As with any alloy, the particular phases and amounts of each present have a direct influence upon its behaviour in any processing step and the properties of the final product.

The phases present at the processing temperatures indicated above can be deduced from Fig. 1. The diagram, taken from Köster and Schmid [4] is an isopleth through their Fe—Co—V ternary space diagram at a constant cobalt composition of 52 wt %. The nominal Remendur composition is indicated on the figure at 2.7 % V.* We utilized Köster and Schmid's results and constructed isotherms of the ternary space diagram at constant temperatures of interest, namely 950, 925 and 900°C. Portions of the 950, 925 and 900°C diagrams are shown in Fig. 2. Although the work of Köster and Schmid does provide useful equilibrium diagram information, their data do not provide precise positioning of the phase boundaries in the regions of interest. Consequently, the diagrams do not permit accurate determination of the amounts of the phases present or their compositions.

This paper reports on the precise determination of five tie-lines in the $\alpha_1 + \gamma$ two-phase

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*This is only an approximate indication since the precise composition is at 2.7 % V on a vertical section through the ternary space diagram at a constant 1/1 composition ratio of iron to cobalt.

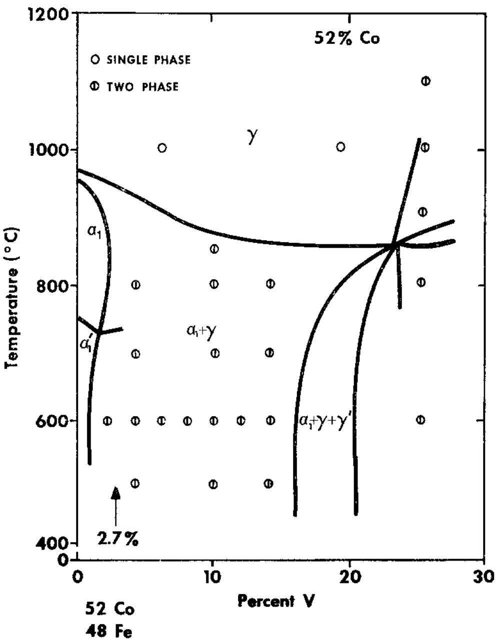

Figure 1 Isopleth through Fe—Co—V ternary phase diagram from work of Köster and Schmid [4].

field in the region of interest, by metallographic and microprobe techniques.

2. Materials and procedure

The two alloys which were used in this investigation were melted and fabricated into rod and wire by Battelle Memorial Institute. Analyses of the alloys by atomic absorption spectroscopy are listed in Table I.

TABLE I Composition of Remendur alloys (wt %)

Alloy	Fe	Co	V	Balance of impurities Mn, P, Ni, C
1	48.27	48.36	2.46	0.91
2	47.34	48.70	2.97	0.99

The alloys are designated as 2.5 and 3.0 % V in the remainder of this paper.

Samples of both alloys in the hot rolled 6.35 mm (0.25 in.) rod were given an equilibrating anneal in flowing Ar-10 % H_2 at either 950, 925 or 900° C for 6 h and subsequently quenched into iced brine (5 % solution of NaCl in water); temperature control of the furnace was ± 2° C. The purpose of the long anneal, as compared to the $\frac{1}{2}$ h commonly used in commercial practice, was to enable the alloys to obtain their equilibrium structure. The protective gas was used, instead of air as in commercial practice, to prevent preferential oxidation of vanadium and iron [5].

Additional samples of the 3.0 % V alloy in both the 925° C-$\frac{1}{2}$ h annealed, 6.35 mm rod condition and after cold drawing to 1.63 mm

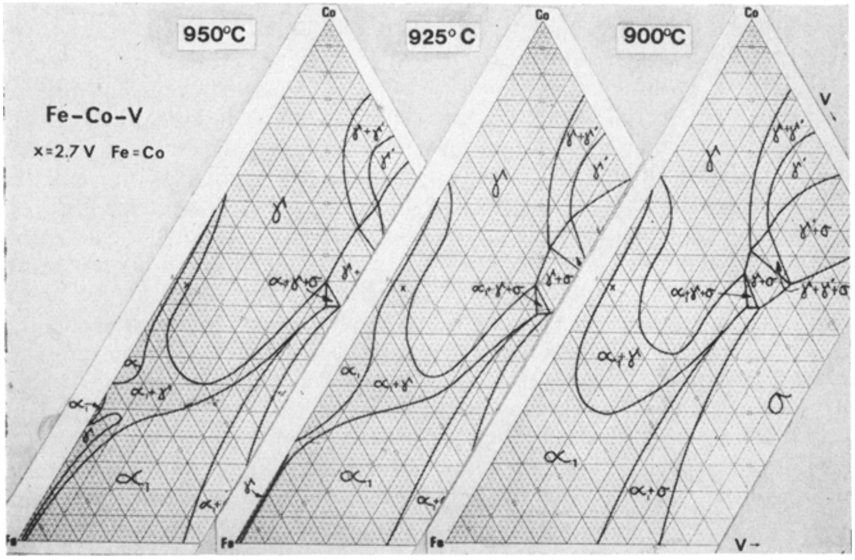

Figure 2 Isotherms of the Fe—Co rich portions of the Fe—Co—V ternary equilibrium diagram constructed from isopleths in the work of Köster and Schmid [4].

(0.064 in.) wire were given an equilibrating anneal in the same gas at 600° C for 96 h. They were cooled to room temperature in the furnace. The purpose of this treatment was to nucleate and grow, large enough for analysis by electron microprobe, the particulate phase which appears at this temperature.

All the experimental samples were mounted, metallographically prepared by routine techniques, and lightly etched (5 to 10 sec) by swabbing with a 5% solution of nitric acid in methyl alcohol (Nital). They were examined and the microstructures photographed with both a Zeiss Ultraphot metallograph employing Differential Interference Contrast (DIC) and a Cambridge Scanning Electron Microscope (SEM). The compositions of the equilibrium phases present in the samples were determined with an SEM-microprobe utilizing both energy-dispersive (qualitative) and wavelength-dispersive (quantitative) techniques.

3. Results and discussion

3.1. Phase equilibrium in the 900 to 950° C range

Fig. 1 indicates that the structure of a 2.7% V alloy at 1100°C is single phase γ(fcc). This phase transforms to a non-equilibrium, vanadium-supersaturated bcc phase, α_2, for rapid (iced-brine quenched) to moderate (air cooled) rates of cooling to room temperature. In the 900 to 950° C annealing range the structure is two-phased α_1 (bcc) + γ which transforms to $\alpha_1 + \alpha_2$ after quenching to room temperature. [1]. Microstructures produced in the 2.5 and 3.0% V alloys by annealing 6 h are shown in Figs. 3 and 4. The Differential Interference Contrast (DIC) mode of illumination emphasizes topographical differences of etched microstructures as if they were illuminated obliquely. In these micrographs the γ phase, which is α_2 at room temperature, appears as a raised feature if one imagines oblique lighting originating at the top of the page.

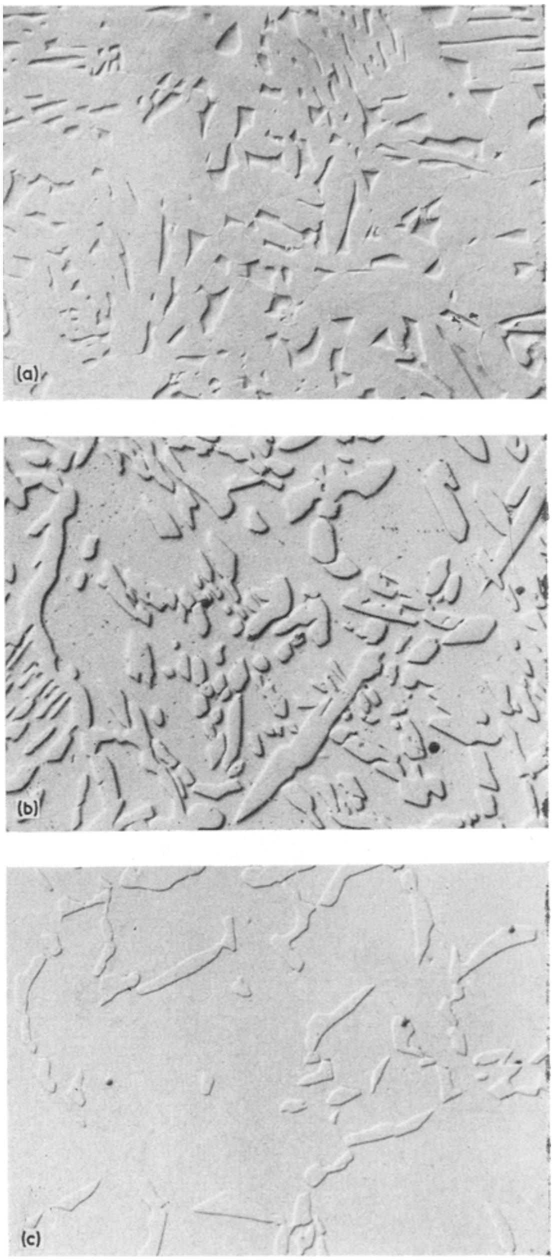

Figure 3 Microstructural differences in the 2.5% V alloy after annealing for 6 h at (a) 950, (b) 925 or (c) 900° C. Etched: DIC (Original magnification: × 600. Reduced 26 % in reproduction).

The figures show that for the 2.5% V alloy there is a complete reversal in the major phase over the relatively small temperature range of 50° C; $\gamma(\alpha_2)$ is predominant at 950° C, whereas α_1 is at 900° C. This is of significance since the precise distribution of the phases after such anneals can affect the ultimate magnetic properties [6]. For the 3.0% V alloy, an annealing temperature of 950° C places it outside of the two-phase field and thus it is entirely γ at temperature. Since an alloy which is entirely $\gamma(\alpha_2)$ is not easily deformed at room temperature by swaging or drawing [1], the practical necessities of maintaining alloy composition and annealing furnace control are obvious. It is also clear that precise positioning of the phase

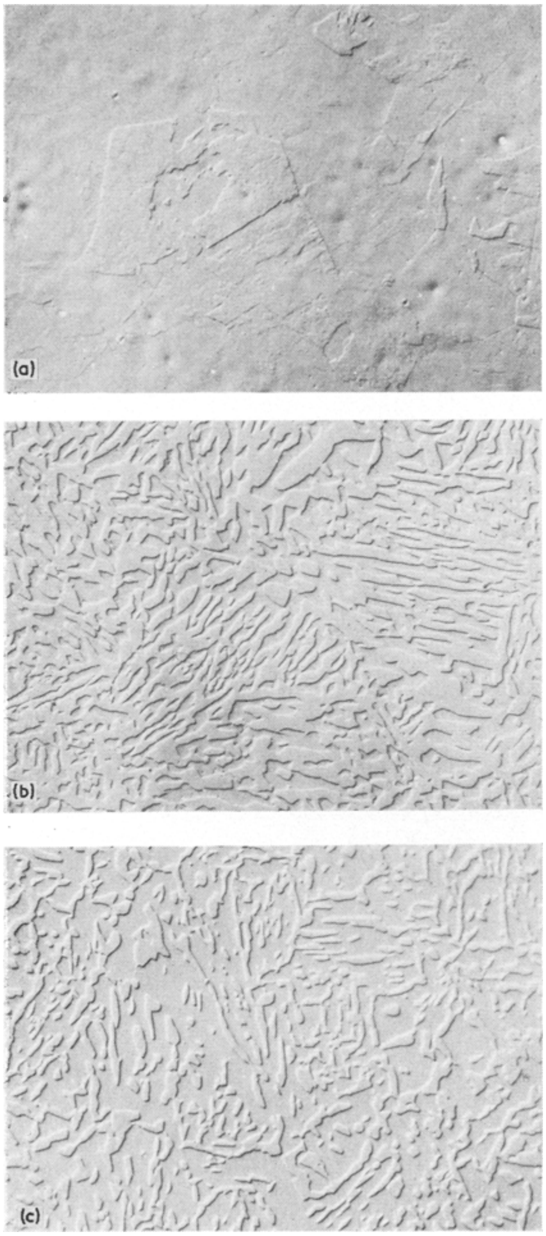

Figure 4 Microstructural differences in the 3.0% V alloy after annealing for 6 h at (a) 950, (b) 925 or (c) 900°C. Etched; DIC (Original magnification: × 600. Reduced 26 % in reproduction).

boundaries in this region is of importance. Since the original work of Köster and Schmid [4] and the reconstructed diagrams (Fig. 2) are only qualitative, further data were required.

For this study compositional analyses of the phases were obtained using an SEM-microprobe on the samples annealed for 6 h. Quantitative analysis was accomplished with the wavelength-dispersive technique utilizing pure elemental standards. Relative X-ray intensities were corrected to composition values with the MAGIC computer program described by Colby [7] and these are given in Table II. The mean chemical compositions were normalized and plotted in Fig. 5 which shows enlargements of portions of the ternary diagrams of Fig. 2. Also drawn in Fig. 5 are dotted lines indicating the extrapolated course of the phase boundaries based upon the quantitative data of this investigation. It was pointed out in earlier work [1] that the microstructures of 2.5 to 3.0% V alloys were exceptionally sensitive to annealing temperature and this was related to the phase diagrams. The revised boundaries further explain this sensitivity. They show the $\alpha_1 + \gamma$ field to be even narrower than expected and the γ-end of the tie-lines to move toward the cobalt corner as temperature decreases.

3.2. Phase equilibrium at 600°C

Ultimately, annealed 0.53 mm (0.021 in.) diameter wire is deformed by stamping and then given a final anneal in hydrogen near 600°C to develop specific magnetic properties. This anneal results in a distribution of fine γ(fcc) particles in a matrix of α_1 (or probably the ordered version α_1' [8, 9]) which remains as the stable structure at room temperature.

Fig. 6 is the complete ternary isotherm at 600°C [4]. It is apparent that the γ composition at 600°C is significantly different from α_1' and also from the γ composition at higher temperatures. In particular, the cobalt content of stable γ is much higher. Fiedler and Davis [10] extracted and collected these second-phase particles by electrolytically dissolving the matrix of a cold rolled sample that had been annealed 48 h at 680°C. The particles were analysed with an atomic absorption spectrophotometer and found to contain 13% Fe, 65% Co, and 22% V by weight.

The 700°C isotherm was also constructed by the authors from the data of Köster and Schmid [4] and is very similar to that for 600°C. Therefore, Fig. 6 may be used to compare the composition of the γ phase as found by Fiedler and Davis in their 680°C anneal. The composition of γ determined by Fielder and Davis is incompatible with this equilibrium diagram.

TABLE II Quantitative microprobe analyses of equilibrium phases*

Temperature (°C)	2.5% V alloy		3.0% V alloy	
	α_1	γ	α_1	γ
950	Co 45.97 ± 0.38	48.11 ± 0.32	—	48.32 ± 0.18
	Fe 50.32 ± 0.33	47.16 ± 0.37	—	47.36 ± 0.23
	V 1.35 ± 0.01	2.61 ± 0.06	—	2.98 ± 0.07
925	Co 46.60 ± 0.16	49.36 ± 0.16	46.28 ± 0.32	49.33 ± 0.14
	Fe 50.03 ± 0.24	45.85 ± 0.25	50.21 ± 0.22	45.96 ± 0.21
	V 1.87 ± 0.03	3.97 ± 0.05	2.13 ± 0.03	4.25 ± 0.09
900	Co 47.37 ± 0.17	50.13 ± 0.17	45.36 ± 0.17	49.35 ± 0.13
	Fe 48.26 ± 0.30	42.91 ± 0.51	49.18 ± 0.21	43.27 ± 0.34
	V 2.19 ± 0.04	4.76 ± 0.03	2.42 ± 0.06	5.29 ± 0.05

*Mean chemical compositions and two sigma limits based on eight analyses.

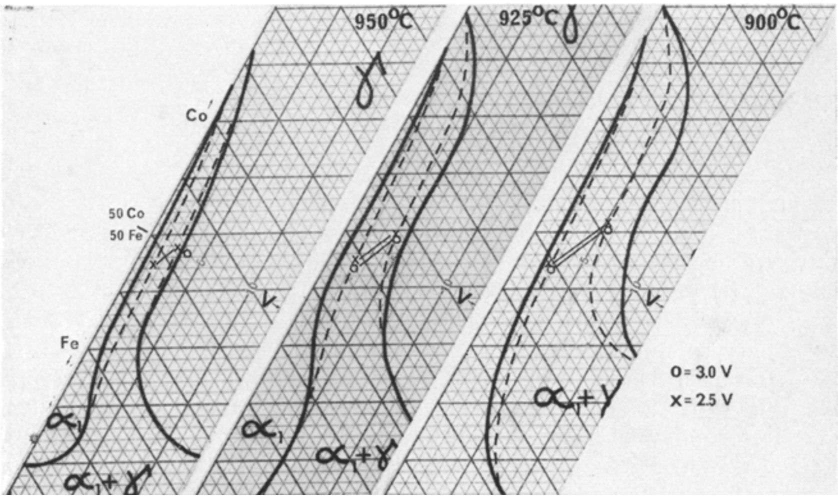

Figure 5 Quantitative determination of segments of the $\alpha_1 + \gamma$ field boundaries in 950, 925 and 900° C isotherms of the Fe—Co—V ternary system.

Their composition for γ falls in the middle of the single phase γ' field which is inconsistent with their alloy composition of 48.8% Fe, 49.0% Co, and 2.2% V. The discrepancy could be due to inherent difficulties in selective dissolution, in the collection of submicron particles, or errors in the original phase diagram work [4].

The longer anneal used in the present work produced the microstructures illustrated in Fig. 7. The more cobalt-rich γ phase appears dark in the optical micrographs and light in the electron micrographs. From the optical micrograph of the 6.35 mm sample (Fig. 7a), it was expected that the γ particles would be large enough for quantitative analysis. However, the corresponding scanning electron micrograph (Fig. 7c) shows the particles are too small for accurate analysis; the electron beam diameter is of the order of 1 µm and the particles are less than 1 µm in their smallest dimension. As can be seen at the higher magnification, the regions which are dark and appear to be single phased in the optical micrograph are actually two phased. The total microstructure can be considered as a matrix of

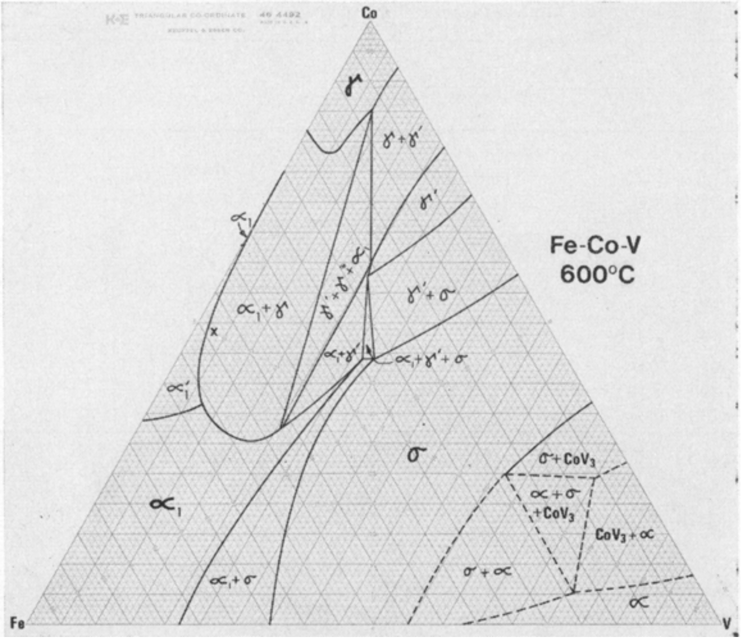

Figure 6 Isotherm of 600°C for the Fe—Co—V ternary equilibrium diagram [4].

primary α_1' containing two-phased regions of secondary α_1' and stabilized γ. This results from the non-equilibrium α_2 phase in the 925°C annealed-and-quenched structure decomposing into two phases, α_1' and γ, upon heating to 600°C.

The effect of deformation, prior to the 600° C anneal, upon the decomposition of α_2 is apparent in Fig. 7b and d. Deformation at room temperature causes a refinement and a redistribution of the α_1 and α_2 phases. Upon subsequent annealing of the cold worked wire at 600°C, the reaction proceeds as described above, i.e. decomposition of α_2 into $\alpha_1' + \gamma$. In this case, however, the resultant microstructure consists of a uniform distribution of submicron γ particles in an α_1' matrix due to the dispersion of the α_2 phase prior to decomposition. Such a microstructure is one which usually enhances coercivity in a ferromagnetic material [11-13] and this has been found in these alloys [6]. However, again the particulate phase was too small for accurate electron microprobe analysis. It is unfortunate that our efforts cannot resolve the discrepancy in the literature concerning the composition of the equilibrium phases at 600 to 700°C. The microprobe results only indicate a significant enrichment of the γ phase in cobalt and vanadium, relative to α_1', which is consistent with both the equilibrium diagram of Köster and Schmid [4] and the analysis of Fiedler and Davis [10].

4. Conclusions

The extreme sensitivity of structure to annealing temperature and vanadium content in the range of 900 to 950°C for Fe/Co/2 to 3 wt % V alloys is attributable to the narrow width of the two-phased $\alpha_1 + \gamma$ region, and the rapid shrinkage of the γ phase field toward the cobalt corner with decreasing temperature. The $\alpha_1 + \gamma$ region is even narrower than indicated in prior published results [4]. For anneals near 600°C, submicron particles of stable Co- and V-rich γ(fcc) form by the decomposition of non-equilibrium α_2 (V-supersaturated bcc) into α_1' (ordered bcc) and γ. The particles of γ were too small for quantitative microprobe analysis and hence, the incompatibility between the phase equilibria data of Köster and Schmid [4] and the γ phase analysis of Fiedler and Davis [10] could not be resolved.

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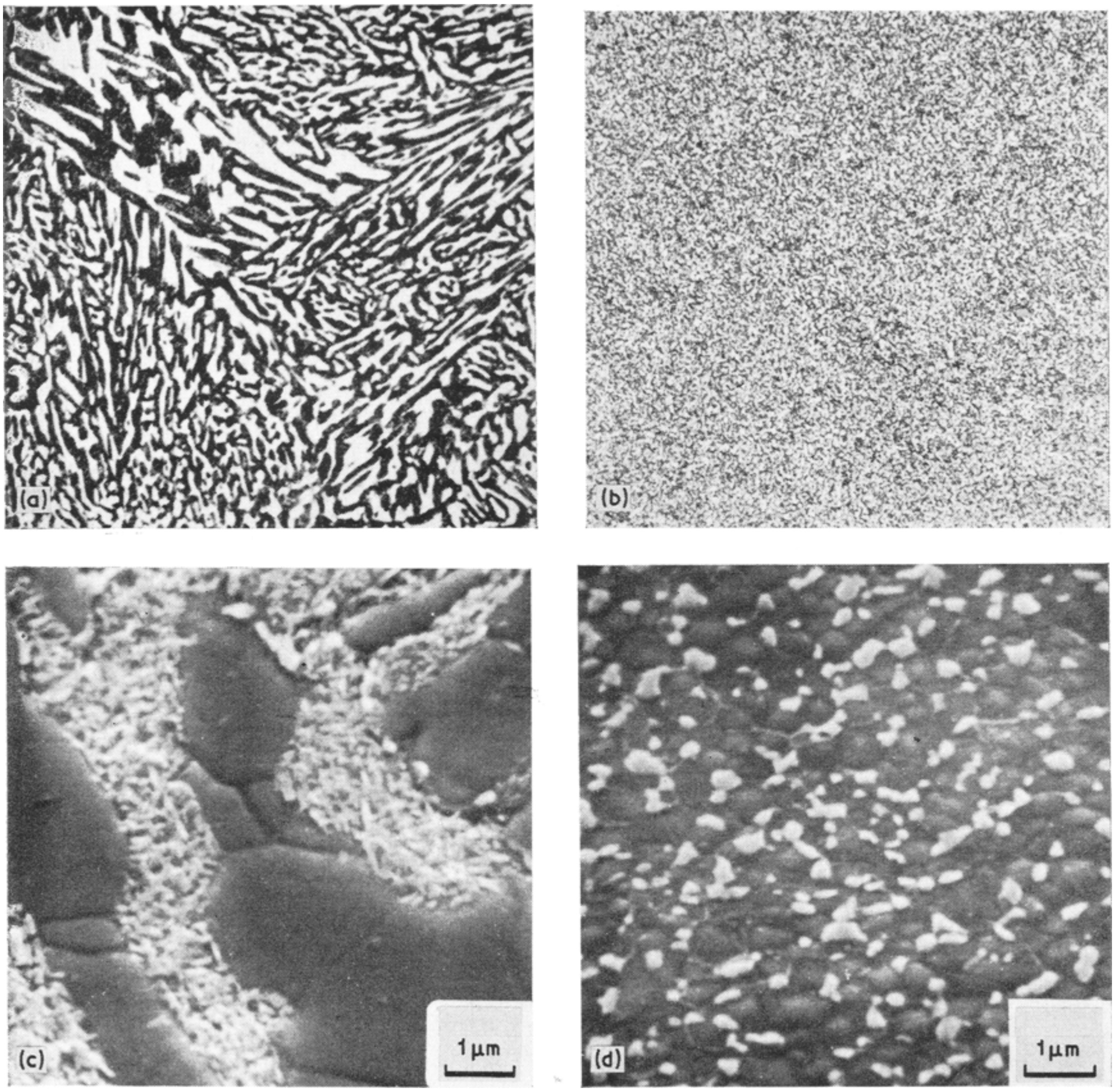

Figure 7 Microstructure of the 3.0% V alloy (925°C annealed 6.35 mm rod and cold drawn 1.63 mm wire) after subsequent annealing at 600°C for 96 h. Etched 5% Nital. (a) 6.35 mm, DIC (× 600). (b) 1.63 mm, DIC (× 600). (c) 6.35 mm, SEM (×10000). (d) 1.63mm, SEM (× 10000. Original magnification indicated: reduced 10.40 % in reproduction).

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References

1. M. R. PINNEL and J. E. BENNETT, *Bell System Technical Journal* **52** (1973) 1325.
2. H. L. B. GOULD and D. H. WENNY, *Elect. Eng.* **76** (1957) 208.
3. K. M. OLSEN, Bell Telephone Laboratories, Murray Hill, N.J. October 1971 (personal communication).
4. W. KÖSTER and H. SCHMID, *Archiv Eisenhüttenw.* **26** (1955) 421.
5. J. E. BENNETT and M. R. PINNEL, Bell Telephone Laboratories, Columbus, Ohio (unpublished research).
6. *Idem, Met. Trans.* **5** (June 1974).
7. J. W. COLBY, "Advances in X-Ray Analysis" (Plenum Press, New York, 1968) pp. 287-305.
8. A. T. ENGLISH, *Trans. Met. Soc. AIME* **236** (1966) 14.
9. N. S. STOLOFF and R. G. DAVIES, *Acta M* **12** (1964) 473.

10. H. C. FIEDLER and A. M. DAVIS, *Met. Trans.* 1 (1970) 1036.
11. R. M. BOZORTH, "Ferromagnetism" (Van Nostrand, New Jersey, 1951) pp. 29-38.
12. D. HADFIELD, "Permanent Magnets and Magnetism" (Wiley, New York, 1962) pp. 62-70.
13. C. KITTEL and J. GALT, "Solid-State Physics" (Academic Press, New York, 1956) p. 437.

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