JOURNAL OF MATERIALS SCIENCE 4 (1969) 25-32

Controlled Solidification of Metal Matrix Composites Utilising Monovariant Eutectic Reactions

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Received 29 April 1968, and in revised form 27 June

The application of monovariant eutectic reactions to the preparation of metal matrix composites is discussed. As is well-known, this class of reactions leads to structures similar to those of an invariant binary eutectic reaction, since in both cases two solid phases precipitate simultaneously from a liquid.

In the case of monovariant eutectics, however, one of these phases is a solid solution. The composition of this solid solution may be varied within wide limits, and a substantial influence on the properties of the matrix and the morphology of the fibres is therefore possible.

As examples, the systems Ag/Au/Si and C/Cr/Ni/Si are used. The former, which has a monovariant ternary eutectic as its only constitutional feature, serves well as a simple demonstration model.

In the C/Cr/Ni/Si system, strengthening of a Cr/Ni/Si matrix (82.25 wt % Ni/11.00 wt % Cr/6.35 wt % Si) by 22 vol % Cr_3C_2 could be achieved by directional solidification.

1. Introduction

It has become clear in the last decade that the presently used materials will not be capable of meeting the requirements of many of the proposed space age devices and systems. Interest has therefore focused, at least for high-temperature applications, on metal matrix composites. Various approaches have been applied to the development of these composites. One of these has been the direct introduction of a stiff, strong, light fibre such as SiC, B, C, etc, into a metal matrix [1-3]. Major problems in this area have been associated with the reactivity of non-metallic filaments with most technologically important metal matrices [4-6].

Another approach, which bypasses the problems associated with the interaction of the filament with the matrix (such as adhesion, bonding, chemical attack, etc) is the preparation *in situ* of intermetallic fibres in a metal matrix by directional solidification of binary eutectics [7, 8].

Excellent results have been obtained in a number of model systems, such as $CuAl_2$ in Al and Al_3Ni in Al. In some cases such as the Al_3Ni/Al system, rod-like as well as blade-like lamellar intermetallic reinforcing phases have been grown into the matrix metal. Composite behaviour has been demonstrated in these systems; they have been used as models to predict the general structural behaviour of metal matrix composites such as tensile and compressive properties, impact resistance, fatigue, etc [9]. It has been difficult, however, utilising binary systems to produce reinforced alloys of major technological importance [10], in particular materials possessing good high-temperature properties.

The major reason for this seems to be the relative inflexibility of the method, a eutectic equilibrium being a point of fixed concentration of all the components. Thus, normally no adjustments in fibre/matrix ratio can be made. It should be pointed out though, that by suitable adjustments of growth rates and temperature gradients in directional solidification experiments "eutectic" structures far from the equilibrium eutectic composition may be achieved [11]. Therefore, this shortcoming of binary eutectics may be overcome. Another severe shortcoming is nevertheless, that no influence on the properties of the matrix can be exerted if a two-component system is used. But the latter is a prime requirement in alloy development, particularly in cases where, besides good mechanical strength, corrosion resistance, oxidation resistance and various other ancillary properties of an alloy require optimisation. Since it is proven that directional solidification of eutectics can be a very suitable method of reinforcement, it is desirable to use a phase reaction of a similar kind which avoids certain of the shortcomings of true eutectic reactions.

It is therefore suggested that monovariant eutectic reactions in higher order systems should be useful for fibre reinforcement by directional solidification methods.

The usefulness of this class of reactions arises from the fact that the final crystallised system appears as a binary eutectic structure but is constituted of a solid-solution matrix and a eutectic precipitate. The structure forms much in the way of a binary eutectic by simultaneous precipitation of two crystallite types, one of which is a solid solution.

It is, of course, clear from an examination of such systems, as presented in various textbooks [12-14], that matrix segregation occurs during the crystallisation process. How severe it is and how to overcome it depends on the actual system in question, but certain complications in experimentally producing such reinforced systems must be expected.

These difficulties should be far outweighed, however, by the advantages monovariant reactions possess compared with true eutectics.

It is immediately clear that the number of systems which can be reinforced is drastically increased. Furthermore, a quite substantial influence on the composition of the matrix can be exerted.

Finally, in certain cases, and within certain limits, the fibre-to-matrix ratio may be variable.

By far the most important possibility here is that of changing the matrix composition. This not only allows optimisation of required properties of the matrix, but also can be very significant as a means of changing the crystallisation behaviour of the fibres, as will be demonstrated below.

2. Experimental Demonstrations of Principles

Although the phase reactions referred to above are well understood and described amply in the literature, it seems advisable to demonstrate some of the properties of alloys so crystallised, by reference to a real system.

The simplest case of such a system, a monovariant ternary eutectic (or eutectic trough), is described by Rhines [13]. This system (Bi/Pb/Sb) is complicated merely by a solid solubility of Bi in Pb.

An extremely simple system of this type is gold-silver-silicon (fig. 1) which serves well as a demonstration model. In figs. 2a-c it can be seen that alloys of extremely varied matrix composition show the same general structure, an apparent eutectic with small amounts of primary crystallisation. It is also clear that in this case the "eutectic" morphology is largely independent of matrix composition.

TABLE I Thermal effects in Ag/Au/Si alloys.

	Composition wt %	Composition at. %	Thermal effects at °C* weak	Thermal effects at °C* strong
Ag	71.0	68.71		
Au	24.0	12.71	857	775, 765
Si	5.0	18.58		
Ag	47.5	51.23		
Au	47.5	28.06	853†	681, 671
Si	5.0	20.71		
Ag	24.0	29.24		
Au	71.0	47.37	557†	538, 525
Si	5.0	23.39		

*All effects were measured on cooling with a rate of ~5° C/min.
Precision of the determination: ± 4° C.
†Very small and uncertain thermal discontinuity.

Table I which shows the thermal effects measured for the three alloys, demonstrates that solid solution segregation should be small because of the minimal separation between solidus and liquidus lines of the trough, which is evident from the close succession of two strong thermal effects in every alloy. In this system not much variation in fibre content is to be expected with a variation of matrix composition, since the eutectic trough runs rather straight.

Finally, owing to the ordering reaction in the Au/Ag solid solution, the properties of the matrix could be influenced by low-temperature ageing treatments as well as by changes in the composition.

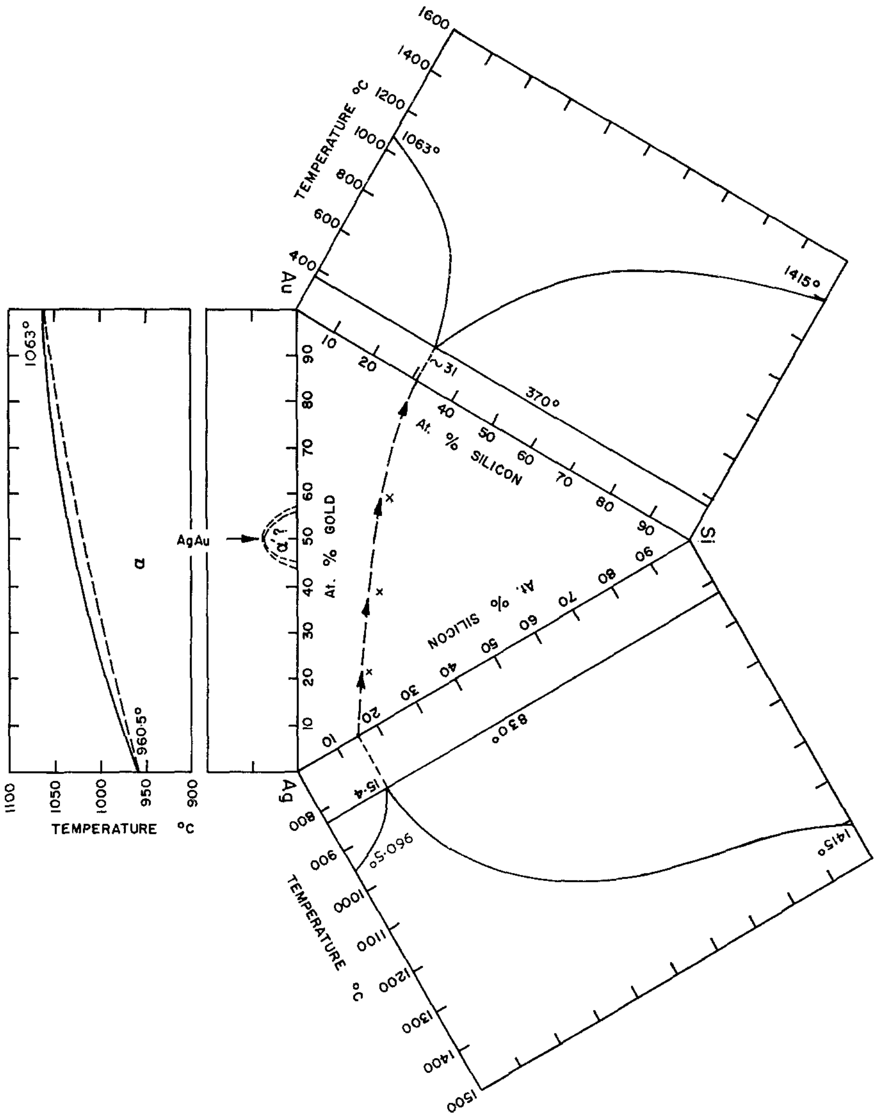


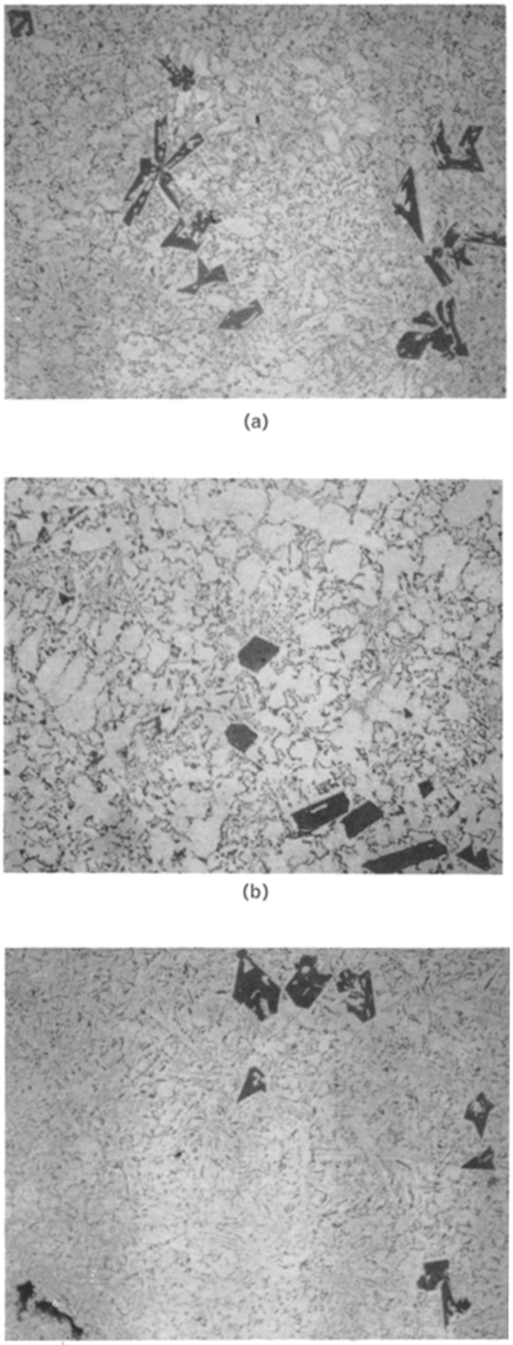
Figure 1 Composite diagram of the Ag/Au/Si ternary system.

Thus, even in this simple system, many of the variables which we believe make "monovariant eutectic" directional solidification so much more flexible, may be readily demonstrated.

3. Carbon/Chromium/Nickel/Silicon Alloys

To achieve more realistic experimental tests of the principles described, an alloy system which contained a monovariant eutectic reaction, and also represented a composition of technological interest,was solidified directionally.The published phase equilibria of the C/Cr/Ni system [15] show that monovariant eutectic reactions dominate the equilibria between all three chromium carbides – Cr_3C_2, Cr_7C_3, and $Cr_{23}C_6$ – and Cr/Ni solid solutions of varied compositions. It is also well known that alloy matrices consisting of nickel with additions of chromium possess desirable high-temperature properties, in particular superior oxidation resistance.

Inspection of the structure of the Cr_3C_2/Cr/Ni eutectic structure unfortunately shows that fibrous growth is most probably impossible because of the undesirable morphology of the monovariant eutectic (fig. 3). This morphology



(a)

(b)

(c)

Figure 2 (a) Microstructure of 47.4 at. % Au/29.2 at. % Ag/23.4 at. % Si. Unetched, polarised light (× 120).
(b) Microstructure of 51.2 at. % Ag/28.1 at. % Ag/20.7 at. % Si. Unetched, polarised light (× 120).
(c) Microstructure of 68.7 at. % Ag/12.7 at. % Au/18.6 at. % Si. Unetched, polarised light (× 120). All alloys are shown "as-cast". All reveal primary crystals of Si.

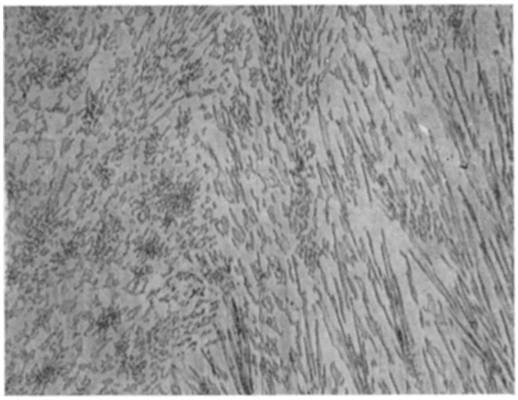


Figure 3 69.64 wt % Ni/27.5 wt % Cr/2.86 wt % C, as-cast, Murakami etch (× 210).

may be modified by additions of Si and the improvement in the structure is obvious (fig. 4).

It is also desirable to maximise the chromium content in the matrix for good oxidation resistance and choose a composition which insures that no undesirable solid-state reactions take place in the material during high-temperature. use.

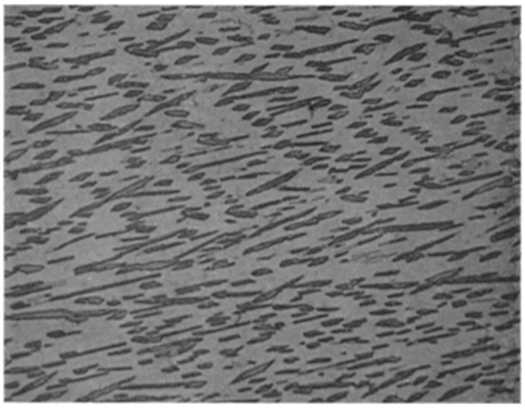


Figure 4 64.64 wt % Ni/27.5 wt % Cr/5 wt % Si/2.86 wt % C, as-cast, Murakami etch (× 210).

Phase equilibrium investigations to find an optimised composition were therefore conducted. They are described in a separate paper [16]. From these investigations an alloy containing 64.64 wt % Ni, 27.50 wt % Cr, 2.86 wt % C, and 5 wt % Si evolved as the most suitable alloy for directional solidification experiments. This alloy contains 22 vol % Cr_3C_2 in a matrix composed of 82.25 wt % Ni, 11.4 wt % Cr, and 6.35 wt % Si.

4. Directional Solidification Experiments

Controlled solidification was accomplished in the simple apparatus shown schematically in fig. 5. Two configurations were used in the solidification experiments: a crucible 10 cm in length by 1.0 cm inside diameter, and a crucible 7.5 cm long by 3.2 cm inside diameter. The diameter of the cooling pedestal in each case matched the outside diameter of the crucible; a thin layer of tin between the crucible and the cooling pedestal was provided to improve heat transfer. Heating was by direct rf coupling to the melt, previous experiments with graphite susceptors having shown the desirability of mixing in the melt by the induction field.

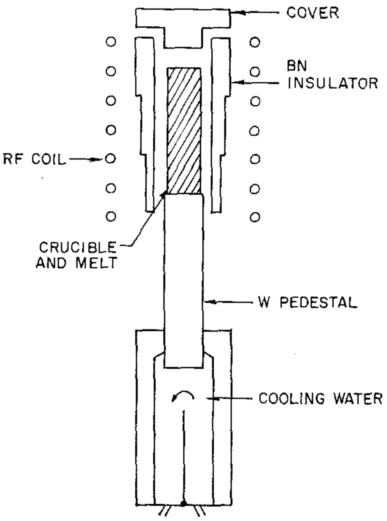


Figure 5 Schematic drawing of directional freezing apparatus.

Directional solidification experiments were done with the small-diameter crucible, and various rf coil configurations and freezing rates from 1 to 10 cm/h. Regardless of the size of the molten zone or the rate of freezing, the ingot showed segregation of the carbide phase at the bottom (i.e. into the solid). The extent of segregation varied somewhat according to the conditions. Thus, when the entire ingot was initially completely melted and the solidification rate was low (1 to 2 cm/h) maximum segregation was produced. Fast solidification with a small molten zone (approximately 10 cm/h and 1.9 cm long) produced a less segregated structure, but the variation in carbide content and structure as a function of position in the ingot was substantial.

The persistence of segregation in the directional solidification experiments led to experiments with normal freezing, since the most regular structures in this material had been observed in small, rapidly frozen buttons. Using the same apparatus, ingots 7.5 cm long by 1.0 cm in diameter were completely melted, superheated by approximately 250° C, then frozen by decreasing the rf power and rapidly increasing the cooling water flow. Freezing rates produced in this manner were in the range of 200 to 300 cm/h. Ingots exhibiting the structure shown in figs. 6a and b could be produced by this technique; however, they were subject to deep shrinkage cavities and pores. Ingots 7.0 cm long by 3.2 cm in diameter frozen in the same way showed less regular structures since the highest freezing rates attained in this configuration were of the order of 150 cm/h.

No attempts were made within the scope of this investigation to produce the high solidification rates which are apparently necessary to overcome the constitutional instability in this particular system to produce perfectly and regularly aligned eutectic structures.

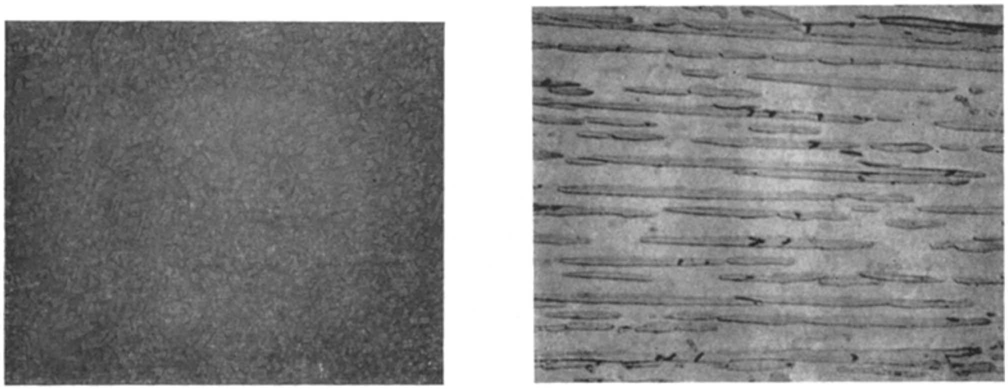
5. Characterisation of Composites

5.1. Crystallographic and Morphological Properties

Fig. 6a is a cross-section of a directionally solidified alloy showing various crystallographic features of the whiskers. A section parallel to the direction of growth, indicating fibre alignment, is shown in fig. 6b.

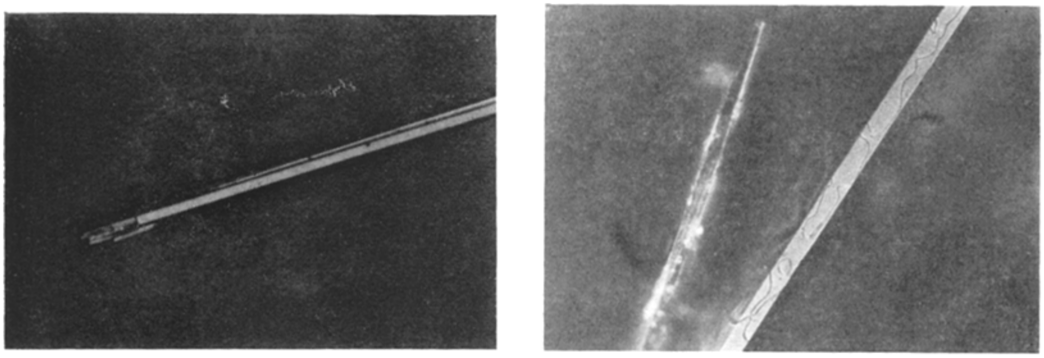
The size, structure, size distribution and crystallographic habit of the Cr_3C_2 crystals were investigated. The extraction of the whiskers from the Cr/Ni/Si matrix was accomplished by dissolution in hot dilute aqua regia for 3 days and in hot concentrated HCl for 1 day. Bundles of well-developed fibres, which were cemented together with a white substance, were obtained after extraction (see fig. 7). Treatment with HF removed the white substance, believed to be SiO_2. X-ray diffraction analysis clearly indicated orthorhombic Cr_3C_2 with lattice constants: $a = 11.48 \pm 0.01$ Å; $b = 5.52 \pm 0.01$ Å; $c = 2.826 \pm 0.005$ Å. These values are in very good agreement with those previously reported [17-19]. It is therefore concluded that Cr_3C_2 does not dissolve significant amounts of Ni or Si into solid solution. This, with respect to Ni, has been previously reported [15].

The fibres have very well defined flat faces



(a) (b)

Figure 6 (a) As-cast 64.6 wt% Ni/27.5 wt% Cr/2.86 wt% C/5 wt% Si, showing cross section of Cr_3C_2 fibres in Ni/Cr/Si matrix (× 120). (b) Section parallel to growth of fibres in alloy of 64.6 wt% Ni/27.5 wt% Cr/2.86 wt% C/5 wt% Si (× 216).



(a) (b)

Figure 7 Bundle of fibres (a) and single fibre of Cr_3C_2 (b) extracted from Ni/Cr/Si matrix by aqua regia, HCl, HF treatment. Single fibre shows surface attack. (a) × 89, (b) × 330.

(as shown in fig. 6a). In cross-section they indicate either orthorhombic or distorted hexagonal habit. The fibre bundle shown in fig. 7a appears to be the original growth configuration. The difficulty in separating individual fibres from this bundle is most probably associated with the formation of insoluble SiO_2 during the dissolution process. Fibres up to 3 to 5 mm long are plentiful, and many single fibres have length to diameter ratios above 100. Interesting surface features have been observed on the single-crystal whiskers. Hexagonal etch pits most probably associated with disordering of the orthorhombic structure have been observed, along with in some cases rather severe erosion patterns (see fig. 7b). These features are felt to be associated with the preferential attack of imperfection boundaries by HF.

5.2. Mechanical Properties

In all samples tested, 85% of the Cr_3C_2 fibres lie within ± 15° of the solidification direction. The Cr_3C_2 reinforced material showed substantial improvement compared with the unreinforced matrix only in the modulus of elasticity. Using the "law of mixtures" relationship, the modulus of elasticity of Cr_3C_2 is calculated to be 60×10^6 psi (1.0 psi = 1.0 lb/in^2 = 7.0×10^{-2} kg/cm^2). This is in reasonable agreement with the reported value of 52×10^6 psi [20]. Typical stress-strain curves of the matrix alloy composition and the Cr_3C_2 reinforced matrix are shown in fig. 8. The test specimens were of flat "dog-bone" type, with a gauge cross section approximately 12.5 mm^2 and a gauge length of approximately 2.5 cm. Measurements were made on an Instron Universal Tester with a strain gauge extensometer. Table II summarises the room temperature tensile properties and table III the room temperature compressive properties of the reinforced structure and the matrix alloy.

Definite load transfer was indicated by fracture of the fibres in the matrix. However, microscopic inspection of fracture surfaces and sections of fracture zones revealed that a small percentage of severely misaligned fibres (oriented 80 to 90° to the growth direction) provided sites for ultimate brittle failure. The reason for the severe misalignment difficulty is believed to be associated with segregation of Si at various points along the freezing front. This belief is based mainly on observations of the profound effect of silicon on the morphology of the carbide phase in the as-cast structures. Little could be done to alleviate this problem under the existing experimental conditions; therefore, studies are presently being carried out at the US Air Force Materials Laboratory to explore alignment by hot extrusion. Also, further work – including careful evaluations of fibre orientation, homogeneity, high-temperature oxidation resistance and high-temperature mechanical properties on the extruded specimens – is planned. These studies, which will be reported in due course, should clearly indicate whether the particular alloy prepared here has significant practical utility.

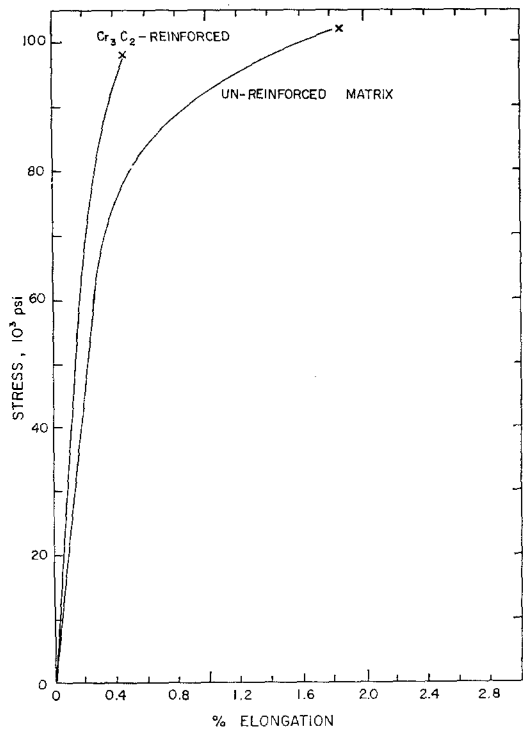


Figure 8 Room-temperature tensile stress-strain curves of 64.6 wt % Ni/27.5 wt % Cr/2.86 wt % C/5 wt % Si and unreinforced matrix alloy.

TABLE II Room temperature tensile properties of $Ni/Cr/Si/Cr_3C_2$ and Ni/Cr/Si.

Property		Cr_3C_2 Reinforced	Matrix
Yield strength (0.1% offset)	psi	86500	75500
	(kg/cm^2)	(6055)	(5285)
Ultimate (fracture) strength	psi	97500	102000
	(kg/cm^2)	(6825)	(7140)
Total elongation %		0.455	1.85
Modulus of elasticity	psi	32.2×10^6	24×10^6
	(kg/cm^2)	(225.4×10^4)	(168×10^4)

TABLE III Compressive strengths of $Ni/Cr/Si/Cr_3C_2$ and Ni/Cr/Si.

Property		Cr_3C_2 Reinforced	Matrix
Yield strength (0.2 offset)	psi	110000	77000
	(kg/cm^2)	(7700)	(5390)
Ultimate strength (fracture)	psi	225000	~220000
	(kg/cm^2)	(15750)	(~15400)
Total strain	%	5.0	~20

From the preliminary mechanical measurements it is nevertheless clear that composite reinforcement was achieved by directional solidification of a monovariant eutectic in an alloy of considerable complexity.

6. Conclusions

The desirability of exploring monovariant eutectic reactions in multicomponent alloys for fibre-reinforcement via directional solidification has been demonstrated. In a complex alloy which may be described as a silicon-modified nichrome composition, Cr_3C_2 fibres were introduced by directional solidification. The alloy, which contained 22 vol % Cr_3C_2 aligned fibres in a matrix consisting of 82.25 wt % Ni, 11.4 wt % Cr, and 6.35 wt % Si, showed "law of mixtures" behaviour as far as the elastic modulus was concerned. However, a small percentage of severely misaligned fibres provide sites for brittle failure in tension and compression. The problems of fibre misalignment are apparently associated with Si segregation during the solidification process. For perfect alignment extremely high solidification rates would be required.

Acknowledgements

The authors would like to acknowledge the financial support of the Advanced Metallurgical Studies Branch, Metals and Ceramics Division, Air Force Materials Laboratory, under Contract USAF No. AF 33 (615)-3106. They would also like to thank Lt W. Meyerer for his valuable technical discussions and encouragement, and Mr R. Stormont and Mr R. Mafera for their experimental assistance.

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