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SUBJECT: DISPERSION STRENGTHENING OF IRON-ALUMINUM BASE ALLOYS:
A FEASIBILITY STUDY

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FROM: Blake King¹

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ABSTRACT

The feasibility of improving the mechanical properties at 1700-1800°F of oxidation-resistant Fe-Al-Cr alloys by means of a refractory dispersion has been explored. A literature search was conducted, preliminary experimental determinations of properties of the alloy and its oxides were carried out, and certain mathematical relations between dispersion characteristics and metallurgical variables were derived. The results indicate that the alloys can be strengthened sufficiently by using a dispersion with an interparticle spacing of about 2-3 μ . High-temperature native oxides of the Fe-Al-Cr alloy consist largely of Al_2O_3 and in theory would serve as a satisfactory second phase.

¹ORINS summer research participant, University of Miami

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DISPERSION STRENGTHENING OF IRON-ALUMINUM BASE ALLOYS:
A FEASIBILITY STUDY

INTRODUCTION

Iron-aluminum base alloys have several characteristics² which make them suitable for use in the fabrication of core components for gas-cooled nuclear reactors. Their oxidation resistance at temperatures of 1800-2000°F is superior to that of any of the usual heat-resisting alloys; they possess a thermal neutron-capture cross section about two-thirds as large as that of the austenitic stainless steels; they are susceptible to attack by acids used in fuel reprocessing; they can be cheaply produced by conventional steel-making techniques;³ and working and joining them does not involve insurmountable difficulties.^{4,5} Their principal disadvantage lies in their marginal high-temperature mechanical properties; these are equivalent to the properties exhibited by straight-chromium stainless steels, but do not approach those of the austenitic stainless steels. In Table 1 the properties of a typical Fe-Al base alloy are compared with those of types 446 and 316 stainless steels; the curves in Fig. 1 make possible at least a qualitative comparison of the creep behavior of Fe-Al base alloys and type 316 stainless steel.

Some success has been achieved in attempts to enhance the high-temperature mechanical properties of Fe-Al base alloys by means of solid-solution

²W. A. Maxwell, B. King, J. Mueller, and N. Ida, "Iron-Aluminum Base Alloys for Reactor Components," Proc. Second United Nations International Conference on the Peaceful Uses of Atomic Energy, 5, 106 (1958).

³V. F. Zackay and E. R. Morgan, "Air Melting of Fe-Al Alloys," Trans. Met. Soc. AIME 212, 203 (1958).

⁴R. Burthwick and S. Goodman, Fe-Al Alloy Systems; Welding of Fe-Al Alloys, WADC Tech. Rep. 57-298, Part 3 (May, 1957).

⁵V. F. Zackay and E. R. Morgan, "Ductile Fe-Al Alloys," Metal Progr. 68, 126 (October, 1955).

Table 1. Properties of 7.5% Al-5% Cr-1% Nb-0.5% Ti-Bal Fe Alloy, and
Certain Other Materials

	Experimental Alloy (Sheet Stock Specimens) ^a	Type 446 Stainless (Wrought Bar Specimens)	Type 316 Stainless (Wrought Bar Specimens)
Room-temperature properties:			
Yield strength (0.2% offset), psi	60,000	51,500 ^b	38,500 ^b
Ultimate tensile strength, psi	87,500	83,000 ^b	85,500 ^b
Elongation, % in 2 in.	24	25	60
Properties at 1500°F:			
Yield strength (0.2% offset), psi	5,000	3,500 ^b	18,500 ^b
Ultimate tensile strength, psi	11,000	8,000 ^b	27,500 ^b
Stress to produce rupture in 1000 hr at 1500°F	1,000	1,000 ^c	7,000 ^c

^a Martin Company Test Data.

^b United States Steel Corporation, ADV-18566 (S).

^c Metals Handbook, 1948.

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Fig. 1. Creep Test Weight - Pan Motion vs Time.

additions.⁶⁻¹² However, the best of the improved alloys cannot compete with the austenitic stainless steels on the basis of high-temperature strength and stability, and it has often been found that alloying of an Fe-Al base material has deleterious effects on its oxidation resistance and room-temperature ductility.

Many investigators¹³ have reported that the creep resistance and high-temperature strength of metals and solid-solution alloys can be improved spectacularly by dispersing in them a fine array of hard particles which are insoluble in the base material in the service temperature range. The characteristics of such dispersion-strengthened materials resemble those of over-aged precipitation-hardened alloys; the advantage of the former lies in the stability of the two-phase structure. The major drawbacks attendant on dispersion strengthening are the difficulties encountered in creating a dispersion having desirable chemical, mechanical, and geometric characteristics, and the fact that the presence of a dispersion in a material usually impairs its ductility and weldability.

The study described in this report was carried out to explore the general feasibility of increasing the high-temperature strength and creep resistance of a family of Fe-Al-Cr base alloys through dispersion effects, and to accumulate information which might be used in the design of dispersion-hardened versions of these alloys.

⁶J. J. Mueller, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Prog. Rep. No. 1, Dec., 1957-Feb., 1958, MND-DB-2521.

⁷J. J. Mueller, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Prog. Rep. No. 2, Mar. 1-May 31, 1958, MND-DB-2522.

⁸F. G. Tate, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Prog. Rep. No. 3, June-August, 1958, MND-DB-2523.

⁹F. G. Tate, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Prog. Rep. No. 4, Sept.-Nov., 1958, MND-DB-2524.

¹⁰F. G. Tate, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Final Report, April, 1959, MND-DB-2525.

¹¹J. F. Nachman and W. J. Buehler, Thermenol, a Non-Strategic Aluminum-Iron Base Alloy for High-Temperature Service, U. S. Naval Ordnance Laboratory, NAVORD Rep. 3700 (June, 1954).

¹²H. A. Saller, J. T. Stacy, and N. S. Eddy, Investigation of Wrought Fe-Cr-Al Alloys for Service at 2200°F, Battelle Memorial Institute, BMI-922 (1954).

¹³R. F. Bunshah and C. G. Goetzel, A Survey of Dispersion Strengthening of Metals and Alloys, WADC Tech. Rep. 59-414 (March, 1960).

The alloys selected for consideration as a base material are quinary compositions based on a 7-1/2 wt % Al-5 wt % Cr-bal Fe alloy; they contain additions of such elements as columbium, titanium, zirconium, and molybdenum. They are thought to represent the best combination of oxidation resistance, ductility, and inherent high-temperature strength.

The undertaking consisted of a literature search, experimental work aimed at determining the properties of the alloy and its oxides which will affect the success with which the material may be dispersion strengthened, and the derivation of certain equations relating dispersion characteristics to controllable metallurgical variables.

EFFECT OF DISPERSION CHARACTERISTICS ON ALLOY PROPERTIES

Bunshah and Goetzel¹³ recently completed a comprehensive review of the technology of dispersion hardening, and include in their report a fairly detailed discussion of the effects of dispersion variables on the properties of strengthened alloys. It is the purpose of this portion of the report to summarize the information that applies to the immediate problem of hardening Fe-Al-Cr alloys, to assess the significance of research reported since this review, and to formulate conclusions regarding the nature of dispersions likely to produce desirable characteristics in an alloy.

Chemical Stability

The ideal dispersant is one that is completely inert with respect to the matrix alloy; the two phases should be mutually insoluble and exhibit no tendency to react with one another. Oxides, nitrides, carbides, and intermetallic compounds have been used as dispersants. Of these, oxides are generally the most satisfactory, and the most desirable oxides are those having the highest negative free energies of formation.

Particle Shape

Dispersed-phase particles can be produced in two shapes; thin platelet particles introduced by surface oxidation of metallic powders which are then consolidated and hot worked to make the final alloy, and equiaxed spherical or quasi-spherical particles resulting typically from internal oxidation of a metal or the mechanical mixing of matrix material and second phase. There seems to be no general agreement concerning the relative desirability

of the two shapes, but it would appear that platelet particles have the more pronounced strengthening effect, while a second phase in the form of spheres results in greater ductility. In the case of the alloy with which this report is concerned, retention of base-alloy ductility is likely to present more of a problem than development of high-temperature strength, so the spherical type of dispersion is possibly the better of the two for this application.

Mechanical Strength of Second Phase

The value of a dispersion is generally agreed to lie in its ability to prevent the motion of dislocations along slip planes and under certain circumstances to inactivate dislocation sources. In consequence, the particles are subjected to rather high stresses. The theory of Orowan¹⁴ regarding the critical shear stress in a dispersion-hardened alloy postulates the existence of particles which will not fracture or deform plastically. A recent theory advanced by Ansell and Lenel¹⁵ holds that yielding of a dispersion-hardened alloy can occur only when the second-phase particles fail in shear. Weertman's¹⁶ explanation of the creep behavior of these alloys necessitates complete integrity of the particles. It can probably be accepted, therefore, that a dispersion of hard, strong particles is desirable.

Particle-Matrix Interfacial Relationships

Two effects must be considered in discussing particle-matrix interfacial phenomena - coherency and wetting. It appears that classical coherence, that is, a tendency of two phases to match lattices with one another, does not occur in the usual dispersion-strengthened alloy. Only one group of investigators¹⁷ has ascribed any coherency effect to a dispersion of the type under discussion; coherency was in this instance proposed as an explanation for the anomalous behavior of 0.005 and 0.01- μ spherical iron

¹⁴E. Orowan, "Dislocations in Metals," Trans. Met. Soc. AIME 131, New York (1954).

¹⁵F. V. Lenel and G. S. Ansell, "A Theory of Dispersion Hardening," (Recent paper to be published in Proc. Met. Soc. AIME, International Powder Metallurgy Conf., June 14, 1960 - sent as an enclosure with a private communication).

¹⁶J. Weertman, Theory of Creep of Dispersion-Hardened Alloys, Metallurgy Division, Naval Research Laboratory, NRL-5123 (April 15, 1958).

¹⁷W. H. Meiklejohn and R. E. Skoda, Dispersion Hardening, Met. and Ceram. Res. Dept., General Electric Research Laboratory, Memo MC-75 (February, 1959).

particles in a solid mercury matrix. It is probable that particles this small cannot be produced easily in an engineering alloy.

Opinion is divided concerning the importance of the wetting action at the interface between the two phases. In true cermet materials, which are furnace-brazed particle aggregates, liquid-phase wetting is clearly essential. Dispersion-hardened metals, however, which contain relatively low second-phase concentrations, may not depend on wetting effects for their properties.

Grant^{18,19} proposes that interphase wetting or coherence may not be necessary in a dispersion-strengthened alloy, and suggests that matrix discontinuities due to the presence of the dispersed phase may be responsible for the strength of the alloy, with the particle-matrix interface acting as a sink for dislocations. In discounting the importance of wetting, he points out that very intimate contact between the two phases can come about as a result of differential thermal contraction of the materials as they are cooled from the temperature at which the alloy was consolidated.

On the other hand, Lenel and Ansell¹⁵ maintain that the nature of the interface must be such that the strain field of an approaching dislocation can be transferred into the structure of the particle, and claim that wetting or adhesion must exist if this is to be accomplished.

At least one investigator²⁰ explains the failure of an attempt to dispersion strengthen an alloy to the presence of void layers around the embedded particles.

If alumina is used as a dispersant in an Fe-Al-Cr matrix, it may well be that true wetting will not occur. Kingery and his co-workers^{21,22} have demonstrated that molten iron will not wet alumina, and it is consequently improbable that the alloy under discussion will wet it either.

A fact of considerable interest in connection with the present discussion is that generally dispersions of intrinsic, grown-in-place oxides have been

¹⁸O. Preston and N. J. Grant, "Dispersion Strengthening of Cu by Internal Oxidation," (Recent paper presented at Metallurgical Society of AIME, 1960 Annual Meeting - sent as an enclosure with private communication, 1960).

¹⁹O. Preston and N. J. Grant, "Dispersed Hard Particle Strengthening of Metals," Trans. Met. Soc. AIME 209, 349 (1957).

²⁰A. W. Cochardt, "Ni-Cr Base Alloys Hardened with Refractory Additions," (Paper presented at Metallurgical Society of AIME, 1957 Annual Meeting).

²¹F. H. Norton et al., Study of Metal-Ceramic Interactions at Elevated Temperatures, USAEC NYO-3144 (Feb. 1, 1953).

²²B. C. Allen and W. D. Kingery, "Surface Tension and Contact Angles in Some Liquid Metal-Solid Ceramic Systems," Trans. Met. Soc. AIME 215, 30 (1959).

found to be quite effective. On the other hand, the results obtained from attempts to introduce foreign oxides into a matrix by mechanical mixing have often been disappointing.²³

It is logical to conclude that while classical interphase coherence or wetting may not be essential in a dispersion-hardened alloy, an extremely intimate contact between the particles and the matrix is desirable to enhance the properties of the alloy. If the two phases produce elastic strains in one another, it is possible that this condition would promote the bonding effect which is needed.

The proper contact between the phases might best be brought about by using a native oxide as a dispersant and employing high-temperature consolidation procedures that would cause the matrix material to compress the particles as it cools. This technique has been found to be successful in many instances, notably in the case of the well-known SAP (sintered aluminum powder) alloys.

Dispersion Morphology Effects

The effect of the geometry of the dispersed phase on alloy properties must be discussed in terms of the interparticle mean free path (λ), also called interparticle spacing, the particle dimension (r or d for spheres, t in the case of platelet particles), and the volume fraction of second-phase material present in the alloy (f). Diagrammatic sketches illustrating these variables will be found on Fig. 2. The empirical and analytical relations thought to exist between dispersion morphology and mechanical properties will be considered below.

Short-Time Mechanical Properties

Several theoretical explanations of yielding phenomena in dispersion-strengthened alloys have been derived to agree fairly well with experimental results. Gensamer²⁴ and his associates rationalized the effects of pearlitic, bainitic, and martensitic dispersions in carbon steel by relating the observed flow stresses to the logarithm of the interparticle mean free path through the ferritic phase. They noted that the flow stress increased as the logarithm λ decreased, and that it seemed to be independent of both the carbon content of the alloy and the nature of the dispersion.

²³E. F. Adkins, C. T. Sims, and R. I. Jaffee, "Nonmetallic Dispersions in Cobalt," Trans. Met. Soc. AIME 215, 344 (April, 1959).

²⁴M. Gensamer et al., "The Tensile Properties of Pearlite, Bainite, and Spheroidite," Trans. Am. Soc. Metals 30, 983 (1942).

SPHERICAL PARTICLES
(AFTER GRANT)

PLATELET PARTICLES

Fig. 2. Relationship Between Particle Size, Volume Fraction, and Mean Interparticle Spacing in a Dispersion-Hardened Alloy.

Orowan¹⁴ applied the dislocation theory and deduced the following relationship between the critical shear stress and certain characteristics of a dispersion-strengthened matrix:

$$\tau = \frac{2cGb}{\lambda} \quad (1)$$

where

τ = critical shear stress,

c = dimensionless constant,

G = shear modulus of matrix alloy,

b = Burgers vector for the active slip system, and

λ = interparticle mean free path.

Lenel and Ansell¹⁵ propose that macroscopic yielding of a dispersion-strengthened alloy must be a consequence of fracture or plastic failure of the second-phase particles. Applying the dislocation theory and noting that the stress required to shear a second-phase particle is proportional to its shear modulus, they derived the following expression which related the yield stress of an alloy to its structural and elastic characteristics:

$$\tau_y = \left(\frac{G_m G_p b}{2c\lambda} \right)^{1/2} \quad (2)$$

where

τ_y = stress to cause macroscopic yielding,

G_m = shear modulus of matrix material,

G_p = shear modulus of second phase,

b = Burgers vector for the active slip system,

c = dimensionless constant, and

λ = interparticle mean free path.

It should be mentioned that Ansell and Lenel attach two major qualifications to their theory. It is valid only when the stress calculated from Eq. 2 is greater than the stress required to activate the Frank-Read sources from which the dislocations originate. Its application is also limited to situations where lines of edge dislocations piled against an array of particles bow out only slightly and have a sufficiently large radius of curvature that they can be considered to be straight. The former limitation also applies to the applicability of Orowan's theory.

Precise experimental verification of such theories is difficult, for several reasons; the considerable scatter that characterizes the results of materials-testing experiments, differences in the degree to which various matrices contribute to strength, and uncertainty in many cases regarding the true magnitude of the interparticle spacing. With a given set of experimental data, it is often possible to plot stresses as functions of the Gensamer, Orowan, or Lenel-Ansell parameters and obtain equally reasonable correlations.

Typical experimental results¹⁸ are shown in Figs. 3 and 4, both of which depict yield strength of dispersion-hardened metals as a function of the negative square root of the interparticle spacing. Figure 3 tends to corroborate Lenel's and Ansell's theory in that the mechanical strength of the particles apparently affects the strength of the alloy, the alumina dispersion contributing greater strength to the alloy, particularly for the larger particle sizes. Also evident is a linear relationship between the strength and the interparticle-spacing parameter. For complete agreement with the Ansell-Lenel theory, however, the two curves should intersect the vertical axis of the plot at a common point.

Illustrated in Fig. 4 are the results of what appears to be the only attempt that has been made to strengthen a ferritic structure by means of an artificial dispersion.²⁵ The interparticle spacings used in plotting the data are very likely in error, having been calculated by approximate methods from sketchy information provided in the referenced paper. In addition, the results should be evaluated in light of the fact the alloys were prepared as part of an exploratory investigation, and are relatively crude; for example, alloys A and B contained approx 27 vol % dispersed Al_2O_3 in the form of comparatively coarse 2- μ particles. It is probable that any dispersion-hardening effect obtained may have been considerably nullified by the reduction of the effective cross sectional area of the specimens tested due to the excessive concentration of Al_2O_3 . However, it does appear that the strengthening effect is related to the interparticle spacing. Of particular interest is the apparent effect of dispersions A and B on the strength of the alloy at 1200°F. The presence of the gross A and B dispersions having wide 3.5- μ interparticle spacings increased the yield strength of the base metal from 4000 psi to approx 28 000 psi. It

²⁵A. Gatti, "Iron-Alumina Materials," Trans. Met. Soc. AIME 215, 753 (1959).

Fig. 3. Room-Temperature Yield Strength as a Function of Interparticle Spacing (Lenel-Ansell Parameter).

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Fig. 4. Yield Strength of Fe-Al₂O₃ Alloys as a Function of Interparticle Spacing (Lenel-Ansell Parameter).

seems that even greater strength increases could have been obtained if the same interparticle spacing could have been preserved with a smaller particle size and a reduced volume fraction of oxide in the alloy.

After analyzing the theories and empirical data discussed above, one arrives at the conclusion that the spacing of particles in a matrix is an important variable governing the strength of a dispersion-hardened alloy, and that strength is related to an inverse function of this interparticle spacing.

Room-Temperature Ductility

As mentioned previously, one of the more difficult problems encountered in the development of useful dispersion-strengthened alloys is the maintenance of satisfactory ductility. The Fe-Al-Cr alloys selected as matrix material for the current study exhibit tensile-test elongations of about 25% at room temperature. For satisfactory workability at room temperature, it is considered that the dispersion-hardened modifications of these alloys should show at least 10% ductility at room temperature.

The curves plotted in Fig. 5 show the effect of interparticle spacing on the room-temperature ductility of dispersion-hardened copper. The tensile ductility of the pure matrix material was reported²⁶ to be 55%. It can be seen from the curve describing the as-extruded Cu + Al₂O₃ alloy that dispersions of particles as widely separated as 2-4 μ cause the elongation to decrease to around 22%, and that finer dispersions bring about even more severe ductility losses. It will be noted also that recrystallization of this alloy resulted in reduced ductility.

An attempt to predict the behavior of a dispersion-hardened Fe-Al-Cr alloy from observations of the properties of dispersion-hardened copper might be dismissed as an exercise in conjecture. However, a conservatively framed conclusion that might be admissible is that a dispersion that causes copper to lose 60% of its ductility is very likely to cause at least that large a loss in the alloys with which this report is concerned. To accept two or three microns as the minimum interparticle spacing for maintenance of ductility in experimental alloys seems to be reasonable.

²⁶K. M. Zwilsky and N. J. Grant, "Dispersion Strengthening in the Copper-Alumina System," (Recent paper presented at Metallurgical Society of AIME, 1960 Annual Meeting - sent as enclosure to private communication, 1960).

Fig. 5. Tensile Elongation of Internally Oxidized Cu-Al and Cu-Si Alloys.

Stress-Rupture Properties

No theory has been evolved to deal specifically with relations between dispersion morphology and the stress rupture properties at elevated temperatures. However, it appears that a relation may exist between the Gensamer parameter ($\log \lambda$) and stress-to-rupture values for a given type of dispersion-hardened alloy.

Typical relationships between stress-rupture values and interparticle spacings are shown by the curves plotted on Figs. 6, 7, and 8. The data presented in these figures were taken from references 27, 28, and 25, respectively. In Fig. 8, the decided effect of the coarse dispersions in alloys A and B is of considerable interest. It will be noted that their presence increases the rupture strength of the base metal by a factor of seven, from about 2000 psi for pure iron to an average of 15 000 psi for the dispersion-strengthened material.

Creep Properties

It is generally accepted that the mechanism by which a particular metal or alloy deforms in creep is a function of stress to which the material is subjected, its service temperature, and the length of time it is loaded. Consequently, it was necessary to make certain assumptions regarding the nature of the service conditions to which a dispersion-hardened Fe-Al-Cr alloy might be subjected in order that information dealing with the probable effect of a dispersion on its creep properties might be deduced.

If the oxidation resistance of the base alloy is to be profitably exploited by using it as the fuel element cladding for gas-cooled reactors, hot-spot temperatures as high as 1750°F may be anticipated, and the metal itself may be heated to around 1800°F (approx 7/10 of its absolute melting temperature).

With regard to tensile stress levels, it is assumed that with careful design these can be held below 3000 psi in suitably supported core components. If a core life of around two years is postulated, its design should be based on steady-state creep rates, and for the dispersion-hardened alloy to be useful it will have to exhibit creep-strain rates certainly no greater than 10^{-6} per hour.

²⁷O. Preston and N. J. Grant, "Dispersion Strengthening of Copper by Internal Oxidation," (Recent paper presented at Metallurgical Society of AIME, 1960 Annual Meeting - sent as enclosure with private communication, 1960).

²⁸E. Gregory and N. J. Grant, "High Temperature Strength of Wrought Aluminum Powder Products," Trans. Met. Soc. AIME 200, 247 (1954).

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Fig. 6. Stress for 100-Hr Rupture Life at 450°C (842°F).

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Fig. 7. Stresses for 100-Hr Rupture Life Commercial SAP-Type Alloys.

Fig. 8. Stresses for 100-Hr Rupture Life of $\text{Fe-Al}_2\text{O}_3$ Alloys at 1200°F.

It would appear that the service conditions for the alloy are to be such that data concerning the steady-state creep behavior of dispersion-hardened alloys at temperatures greater than $0.5 T_m$, under low stress, and at small strain rates would apply in the present case.

The details of the structural alterations sustained by a metal in creep under these conditions of temperature and stress will not be discussed in this report, as there is impressive agreement among those engaged in studying high-temperature ($T > 0.5 T_m$) creep phenomena.^{29,30} The basic mechanism involves recovery through the climb of dislocations, which in turn is a process that depends on the diffusion of vacancies toward or away from dislocations. The more detailed and specific creep equations to be discussed subsequently in this report are, in their general form, consistent with Schoeck's relatively simple mathematical rate expression:

$$\dot{\epsilon} = Ae^{\frac{-Q}{RT}} \quad (3)$$

where

$\dot{\epsilon}$ = strain rate;

A = a function of stress, temperature, and the structural characteristics of the material;

Q = an activation energy which may be a function of stress, temperature, and structure;

e = the Napierian base;

R = gas constant; and

T = absolute temperature.

Weertman³¹ has attempted a detailed analysis of the creep behavior of dispersion-strengthened metals and has succeeded in deriving a group of expressions relating steady-state creep strain rates to the pertinent structural and environmental variables. As far as is known, his is the only effort in this field which has met with any success, and in his general approach to the problem Parker and Dorn²⁹ seem to be in agreement.

Weertman postulates the following as a basis for his theories: a uniform array of particles in an infinite matrix; a natural three-dimensional dislocation network which affords Frank-Read sources of length L, or, alternatively,

²⁹G. Schoeck et al., Creep and Recovery, American Society for Metals, 1957.

³⁰I. Finnie and W. R. Heller, Creep of Engineering Materials, pp. 64-89, McGraw-Hill, New York, 1959.

³¹J. Weertman, Theory of Creep of Dispersion-Hardened Alloys, Metallurgy Division, Naval Research Laboratory, NRL-5123 (April 15, 1958).

Frank-Read sources of length λ between the second-phase particles; and a creep model involving the climb of expanding dislocations or "pinched off" loops over the particles. The two cases considered by Weertman are pictured on Fig. 9.

At shear stresses greater than those necessary to activate a Frank-Read source of length L and less than those required to force dislocations between the particles barring their progress across the slip plane, dislocations climb over the obstacles to neighboring slip planes where they continue to move or are annihilated by other dislocations of opposite sign. Weertman deduces the low-stress creep rate to be:

$$\dot{\epsilon} = \frac{\pi}{2k} \frac{b^3 \tau}{T d^2} A e^{-\frac{Q}{RT}}, \quad (4)$$

where

- $\dot{\epsilon}$ = strain rate,
- b = Burgers vector for the active slip system,
- k = Boltzmann's constant,
- τ = shear stress,
- T = absolute temperature,
- d = particle diameter,
- A = a frequency factor,
- Q = an activation energy, and
- R = gas constant.

An approximate estimate of the maximum tensile stress which can exist in a ferritic alloy for Eq. 4 to apply can be calculated from the Gb/λ criterion in Eq. 1. If a shear modulus of 7×10^{10} dynes/cm², a Burgers vector of 3×10^{-8} cm, and an interparticle spacing of 2μ (2×10^{-4} cm) are assumed, a resolved shear stress of about 10^8 dynes/cm² appears to be the upper limit of Weertman's low-stress region. The corresponding engineering tensile stress is approx 4000 psi.

Weertman's high-stress creep mechanism is shown on the right-hand side of Fig. 9; edge dislocations originating at a Frank-Read source are swept between the particles leaving behind dislocation loops surrounding islands of unslipped material in which the particles are centered. The loops then climb under or over the particles, extinguishing themselves and relieving the back-stress on the

$$\dot{\epsilon} = \frac{\pi}{2k} \frac{b^3 \tau}{T d^2} A e^{-Q/RT} ,$$

$$\text{for } \frac{Gb}{L} < \tau < \frac{Gb}{\lambda} .$$

Variables:

b = Burger's Vector, cm

k = Boltzmann Constant, dyne cm/°K

τ = Shear Stress, dynes/cm²

T = Temperature, °K

d = Particle Dia., cm

A = Frequency Factor, cm²/sec

Q = Activation Energy, cal/mole

R = Gas Constant, cal/mole °K

G = Shear Modulus, dynes/cm²

$\dot{\epsilon}$ = Strain Rate, per second

$$\dot{\epsilon} = \frac{2\pi}{k} \frac{\tau^4 \lambda^2}{d G^3 T} A e^{-Q/RT} ,$$

$$\text{for } \frac{2\tau^2 \lambda b^2}{GkT} \leq 1 .$$

$$\dot{\epsilon} = \frac{\pi \tau^2 \lambda}{G^2 b^2 d} e^{2\tau^2 \lambda b^2 / GkT} A e^{-Q/RT} ,$$

$$\text{for } \frac{2\tau^2 \lambda b^2}{GkT} > 1 .$$

Fig. 9. Steady-State Creep Through Dislocation Climb (After Weertman).

original slip plane. Weertman finds two equations to be necessary for the description of strain rates at stresses great enough to cause the pinching-off effect:

$$\dot{\epsilon} = \frac{2\pi}{k} \frac{\tau^4 \lambda^2}{dG^3 T} A_e^{-\frac{Q}{RT}} \quad \text{for } \frac{2\tau^2 \lambda b^2}{GkT} \leq 1 \quad (5)$$

$$\dot{\epsilon} = \frac{\pi^2 \lambda}{G^2 b^2 d} e^{2\tau^2 \lambda b^2 / GkT} A_e^{-\frac{Q}{RT}} \quad \text{for } \frac{2\tau^2 \lambda b^2}{GkT} > 1 \quad (6)$$

where the variables are the same as those defined for Eq. 4.

An appreciation of the stress levels existing in ferritic structures when these expressions apply can be obtained by setting the new criterion-quantity equal to unity and solving for τ . Using the same values for modulus, Burgers vector, and interparticle spacing as those employed in the preceding calculation, and assuming a temperature of 1200°K, the shear stress τ is found to be about 6×10^8 dynes/cm². The tensile stress in the material would then be roughly 20 000 psi. At the proposed service temperature, Eq. 5 would hold for stresses below 20 000 psi, and Eq. 6 for stresses greater than this.

Three groups of investigators have attempted to test the validity of Weertman's equations by comparing experimentally determined creep rates with those predicted by the theory.

Ansell and Weertman³² conducted creep tests on MD-2100, a SAP-type aluminum alloy containing about two volume percent of Al₂O₃ in the form of thin platelets; the average interparticle spacing was approx 0.5 μ . The material was tested in the as-extruded condition and after it had been given a recrystallization heat treatment.

The as-extruded material tested at 673-873°K (0.7-0.9 T_m) under stresses ranging from 1.4×10^7 to 6.27×10^8 dynes/cm² exhibited creep rates greatly different from those calculated from the theory. The discrepancies are explained as resulting from the fact that the grain size in the material was about the same as the interparticle spacing. The presence of grain boundaries is not considered by the theory. The authors propose that in this particular material the grain boundaries acted as sources for dislocations.

³²G. S. Ansell and J. Weertman, "Creep of a Dispersion-Hardened Aluminum Alloy," Trans. Met. Soc. AIME 215, 838 (1959).

The recrystallized material was tested at the same temperatures and at stresses between 7×10^6 and 3.5×10^8 dynes/cm². No steady-state creep could be detected. It is theorized that the large recrystallized grains were essentially free of active dislocation sources, and the grain size of the alloy was large enough so that the presence of grain-boundary material could not have had a great effect on the behavior of the alloy.

Ansell³³ explains this apparent sparsity of dislocation sources by proposing that the movement of grain boundaries during extrusion of SAP-type alloys sweeps both dislocations and Frank-Read sources into the vicinity of the second-phase particles where they are pinned in place and deactivated. The resultant alloy is nearly free of active dislocation sources and the usual three-dimensional dislocation network. Deformation then requires that dislocations be nucleated in the grain boundaries, and this necessitates large stresses even at elevated temperatures; at low to moderate stresses, no steady-state creep need occur.

If Ansell is correct in his contention, two possibilities present themselves. The first is that the ductility problem associated with SAP-type alloys might be alleviated by pinning only a portion of the dislocation sources. This could be accomplished either by using a coarser dispersion than that characteristic of SAP materials or by less severe hot working of the alloys during extrusion. The second is that it may be possible with the SAP process to produce recrystallized dispersion-strengthened alloys that will exhibit no secondary creep at all at low to moderate stresses on the order of Gb/λ .

In more recent experiments, Lenel and Ansell³⁴ obtained results which tend to corroborate some aspects of Weertman's theory. Two recrystallized SAP-type alloys containing somewhat coarser dispersions than that of MD-2100 were tested; RP-15-30, having a mean interparticle spacing of 6 μ , and AT-400, with a mean interparticle spacing of 1 μ . The experimental data, together with the creep rates predicted by Weertman's equations, are shown on Fig. 10. The results of theory and experiment differ by several orders of magnitude, but it is encouraging to note that the strain rates vary as the fourth power of the applied stress and approximately as the square of the interparticle spacing, in accordance with the theory.

³³G. S. Ansell, A Proposed Mechanism for Strengthening SAP-Type Alloys, Metallurgy Division, Naval Research Laboratory, NRL-5206 (October 7, 1958).

³⁴F. V. Lenel and G. S. Ansell, "A Theory of Dispersion Hardening," (Recent paper to be published in Proc. Met. Soc. AIME, International Powder Metallurgy Conference, June 14, 1960 - sent as an enclosure with a private communication, 1960).

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Fig. 10. Steady-State Creep of Recrystallized Al- Al_2O_3 Alloys
(After Lenel and Ansell).

Adachi and Grant³⁵ tested recrystallized Cu-SiO₂ and Cu-Al₂O₃ alloys and observed creep to occur in each instance. On the basis of these results they take exception to the contention of Weertman and Ansell³² that there are practically no active dislocation sources in a recrystallized SAP-type alloy. It is possible, however, that the two sets of data may not be contradictory. Ansell theorizes, as noted previously, that coarse dispersions may not inactivate all the dislocation sources in a grain. The MD-2100 alloy contained an ultrafine dispersion with a mean interparticle distance of about 0.5 μ ; the five alloys of Adachi and Grant, on the other hand, had dispersions with particle separations ranging from 0.8-8.1 μ . The minimum tensile stress to which the alloy containing the 0.8- μ dispersion was subjected was about 12×10^8 dynes/cm²; the resolved shear stress was therefore about 4.5×10^8 dynes/cm², two to three times as great as the Gb/λ stress below which creep seems not to have been observed. These facts would indicate that the behavior of Adachi's and Grant's alloys can more reasonably be compared with that of Ansell's and Lenel's RP 15-30 and AT-400, which were also observed to creep. It might be proposed that only very fine dispersions can give rise to the no-creep effect noted by Ansell and Weertman.

It might be proposed that Weertman's theories define the maximum creep rates that a dispersion-strengthened alloy will exhibit. Weertman considers only the effect of the dispersion on the mobility of dislocations, whereas in an actual material there may exist other obstacles to their motion. The presence of such things as Cottrell or Suzuki impurity clouds, sessile dislocations, and subgrain boundaries also serves to inhibit dislocation travel. Possibly some success might be had in superimposing on Weertman's dispersion-effect theory the results of his analysis of creep in a material in which Lomer dislocations act as barriers to dislocation motion.³⁶

Grant and his associates, after an extensive study of the creep properties of over-aged Al-CuAl₂ alloys at temperatures greater than 0.5 T_m,^(ref 37)

³⁵M. Adachi and N. J. Grant, "The Effects of Stored Energy on the Creep Rupture Properties of Internally Oxidized Cu-Alumina and Cu-Silica Alloys," (Recent paper presented at Metallurgical Society of AIME, 1960 Annual Meeting - sent as an enclosure to private communication, 1960).

³⁶J. Weertman, "Theory of Steady-State Creep Based on Dislocation Climb," J. Appl. Phys. 26, 1213 (October, 1955).

³⁷R. M. N. Pelloux, A. R. Chandhuri, and N. J. Grant, "Creep Deformation of Al-Cu Two Phase Alloys," Trans. Met. Soc. AIME 215, 204 (1959).

concluded that a dispersion is most effective in inhibiting high-temperature creep of a pure metal or solid solution if (1) along the grain boundaries the second phase is in the form of large, widely-spaced particles to prevent grain-boundary shear and migration; (2) the grain boundaries themselves are not regular, but jagged; and (3) within the grains, the second phase is in the form of very closely spaced particles.

Other Particle Effects

Two corollary effects of the presence of second-phase particles may exist. Geisler³⁸ points out that the effective size of a coherent particle can be larger than the actual particle dimension, the strained region in the surrounding matrix acting to augment the effect of the particle. To a degree, the same mechanism may obtain in the case of incoherent artificial dispersions if the two phases subject one another to elastic strains.

Grant and his coworkers^{35,39} ascribe a good portion of the strength of SAP-type alloys to work-hardening of the material during the extrusion process. It is considered that the presence of the dispersion makes it more difficult for the strain energy stored in the material to be released through recovery processes.

Volume Concentration of Second Phase

Interparticle spacing seems to be the parameter to which the mechanical properties of a dispersion-hardened alloy can be most directly related, and in terms of which they are usually reported. Since, as will be shown in a following section of this report, volume fraction, particle size, and interparticle spacing are not mutually independent variables, it is somewhat difficult to correlate mechanical characteristics directly with the volume fraction of the second phase in an alloy. However, there is some evidence that would make it appear desirable to introduce the least possible amount of a foreign substance into an alloy.

Gatti's alumina-strengthened iron-matrix alloys⁴⁰ exhibited disappointingly low ductilities at room temperature. These materials contained from 15-27 vol % Al_2O_3 , and their microstructures were somewhat similar to those of classic cermets. It is theorized that the ductility of the alloys, as well as their strength, might have been enhanced had it been possible to maintain effective interparticle spacings with the use of less Al_2O_3 . The results of the work

³⁸A. H. Geisler, Phase Transformation in Solids, p. 387, Wiley, New York, 1951.

³⁹O. Preston and N.J. Grant, "Dispersion Strengthening of Copper by Internal Oxidation," (recent paper presented at Metallurgical Society of AIME, 1960 Annual Meeting - sent as an enclosure with private communication, 1960).

⁴⁰A. Gatti, "Iron-Alumina Materials," Trans. Met. Soc. AIME 215, 753 (1959).

of Grant and his associates^{39,41} with dispersion-strengthened copper seem to indicate that the benefits derived from the presence of a dispersion seem to drop off at second-phase concentrations on the order of 10 vol %. It is perhaps significant to note that while the original SAP alloy contained 10-14 vol % Al_2O_3 ,^(ref 38) there is a trend in recent years to reduce the oxide content of dispersion-strengthened aluminum alloys to volume fractions well under 10%.

Conclusions Regarding Dispersion Characteristics

The results of the literature survey described on the preceding pages are thought to justify the following conclusions regarding the nature of a dispersion which would impart desirable properties to an Fe-Al-Cr base alloy:

1. Chemical and physical stability of the dispersant is essential.
2. A dispersion in the form of quasi-spherical particles would probably be best from the standpoint of maintaining the ductility of the base alloy, while a dispersion of platelets might have a more pronounced effect in enhancing high-temperature strength.
3. The second-phase particles must possess considerable mechanical strength.
4. Intimate mechanical contact, or a bonding effect, between the particles and the matrix is required.
5. An upper limit of 3-4 μ must be placed on interparticle spacing if the desired high-temperature properties are to be realized, while the necessity for maintaining ductility dictates a minimum interparticle spacing of from 2-3 μ .
6. The presence of relatively large particles fixed in the grain boundaries of the matrix is desirable to inhibit grain-boundary migration and shear contributions to creep deformation.
7. The volume fraction of dispersant introduced into the alloy should be kept at a minimum consistent with producing the necessary interparticle spacings.

PROPERTIES OF THE BASE ALLOY

The mechanical and chemical properties of the base Fe-Al-Cr alloy which must be considered in designing and fabricating a dispersion-hardened version of the material have been examined. The specific factors which have been assessed and the conclusions which were arrived at as a result of the study are described in this section of the report.

⁴¹K. M. Zwilsky and N.J. Grant, "Dispersion Strengthening in the Copper-Alumina System," (recent paper presented at the Metallurgical Society of AIME, 1960 Annual Meeting - sent as enclosure to private communication, 1960).

Mechanical Characteristics

It is thought that three properties of the Fe-Al-Cr alloy have a particular bearing on the present problem; its ductility, its inherent creep resistance, and its susceptibility to present powder-preparation methods.

Ductility

A persistent source of difficulty in the development of useful Fe-Al base materials has been the fact that aluminum additions sufficient to impart oxidation resistance to an alloy also tend to make it brittle. Nine to eleven percent aluminum must be present in a binary Fe-Al alloy to give good oxidation resistance,⁴² but most investigators have discovered that ductility is reduced severely when more than 7.5 wt % of aluminum is present in a binary.⁴²⁻⁴⁸ In the case of the Fe-Al-Cr ternary suggested as a matrix material in the present undertaking, the aluminum content has been reduced to a level at which it will not detract too much from the ductility of the alloy, and chromium has been added to provide compensatory oxidation resistance.

It has been brought out previously in this report that the addition of a dispersion to an alloy has an unfortunate, and apparently unavoidable, deleterious effect on its ductility. It is to be hoped that tensile ductilities at least as great as 10% can be maintained in the dispersion-strengthened Fe-Al-Cr base. Should this be found not to be possible, however, a more ductile matrix alloy might be made by reducing its aluminum content to around 6 wt % at the expense of some sacrifice of oxidation resistance.

⁴²A. Von Zeerleder, "The Sintering of Aluminum Alloys," Z. Metallkunde 41, 228 (1950).

⁴³V. F. Zackay and E. R. Morgan, "Ductile Fe-Al Alloys," Metal Progr. 68, 126 (October, 1955).

⁴⁴J. J. Mueller, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Prog. Rep. No. 1, Dec., 1957-Feb., 1958, MND-DB-2521.

⁴⁵J. J. Mueller, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Prog. Rep. No. 2, Mar. 1-May 31, 1958, MND-DB-2522.

⁴⁶F. G. Tate, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Prog. Rep. No. 3, June-August, 1958, MND-DB-2523.

⁴⁷F. G. Tate, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Prog. Rep. No. 4, Sept.-Nov., 1958, MND-DB-2524.

⁴⁸F. G. Tate, Development of Fe-Al Base Alloys for Gas-Cooled Reactor Components, Martin Company Final Report, April, 1959, MND-DB-2525.

Creep Resistance

Probably the most attractive feature of the dispersion-strengthening mechanism is the phenomenal enhancement of creep and stress-rupture properties it makes possible; improvements measurable in terms of orders of magnitude can be brought about by means of ultrafine dispersions.

It is suggested, however, that such drastic alteration of properties is not necessary in the case of the present alloy. Reference to Table 1 indicates that only about a seven-fold increase in stress-rupture strength is necessary to duplicate the properties of type 316 stainless steel, and it is encouraging to note (Fig. 8) that this can be attained with a relatively crude dispersion.

If the curves plotted on Fig. 1 can be taken to represent the relative creep behavior of Fe-Al-Cr alloys and type 316 stainless steel, it is apparent that the deformation rate of the experimental alloys is only about three times that of the conventional stainless material. In view of the results obtained in dispersion hardening other alloys, it is considered reasonable to expect that the required improvement of Fe-Al-Cr can be brought about by means of a relatively minor dispersion effect.

It must be borne in mind, however, that the relative improvement in properties obtained by superimposing a dispersion-hardening mechanism on an alloy already somewhat strengthened by solid-solution effects is not likely to be as impressive as that realized in hardening a pure metal such as aluminum, copper, or iron.

Powder-Preparation Considerations

A reasonable familiarity on the part of the reader with the principal techniques employed in making dispersion-hardened alloys has been assumed, and it has not been explained that they are usually based on powder-metallurgy procedures.

It is anticipated that some difficulty may be encountered in economically producing Fe-Al-Cr powders in composition ranges suitable for use as matrix alloys. The alloys are too ductile to be successfully pulverized by milling, and their melting point is so high (approx 2800°F) that gas-blast atomization is hardly feasible. Chemical methods, such as reduction, are slow and expensive.

Advantage may be taken of the brittleness of alloys containing more than 7.5 wt % Al, however, to make a master-alloy composition that can be fragmented mechanically. This powder could be blended with elemental or ferroalloy powders, and the matrix of the final product homogenized if necessary, by suitable heat treatment after compaction and extrusion.

A water-atomized Fe-Al-Cr powder obtained for experimental purposes proved to be too brittle to be useful and was found to contain 1.06 wt % O_2 . Its porous microstructure was an indication that considerable internal oxidation had occurred and that an exceedingly fine dispersion exists in the material.

Chemical Characteristics

It was brought out in a preceding portion of this report that intrinsic oxides, those native to an alloy, seem to make desirable second-phase materials. It is fortuitous that the oxides formed on both Fe-Al binaries and Fe-Al-Cr ternary alloys, particularly at higher temperatures, have mechanical and chemical properties that should make them effective as dispersants.

There is some reason to believe that oxides formed on binary alloys at temperatures greater than 2000°F are predominantly Al_2O_3 .^(refs. 49,50) The aluminum apparently acts to reduce any iron oxides that form, though these are usually present in sufficient quantity to color the oxide film.

According to Kornilov, a Russian investigator whose results are summarized by Case and Van Horn,⁵⁰ oxides are formed on ternary Fe-Al-Cr alloys at temperatures below 1290°F through the following reaction:

In this temperature range, the three oxides exist together as a solid solution. At temperatures in excess of 1290°F, the two reactions shown below take place simultaneously with the one described previously, and the compositions of the film tends to change to Al_2O_3 :

In order to check this information, coupons were prepared from 0.030-in.-sheet stock rolled from an extruded alloy having the following composition:

⁴⁹C. Sykes and J. W. Bampfylde, "The Physical Properties of Iron-Aluminum Alloys," J. Iron Steel Inst. 130,389 (1934).

⁵⁰S. L. Case and K. R. Van Horn, Aluminum in Iron and Steel, pp. 297-310, Wiley, New York, 1953.

Al	7.52 wt %
Cr	4.90 wt %
Cb	0.98 wt %
Ti	0.50 wt %
C	0.065 wt %

These coupons were exposed to still air in a combustion furnace at temperatures ranging from 820-1800°F for from 10 min to 4 hr.

The oxide films were analyzed by the ORNL Analytical Chemistry Division using transmission and reflection electron-diffraction techniques. The results of these analyses given in Table 2 in general tended to corroborate Kornilov's except that the presence of Cr_2O_3 was not detected.

The data in Table 2 and Kornilov's results indicate a possible source of difficulty. It is probable that oxide film less than 0.1μ thick will be desirable if a modification of the SAP process is used to prepare the dispersion-hardened alloy. It seems, however, that high-alumina films can be grown only by exposing the metal to high temperatures for fairly extended periods, and the resulting film thicknesses are on the order of 0.2μ .

Table 2. Characteristics of Oxides Formed on Fe-Al-Cr Alloy

Exposure		Composition as Determined by Electron Diffraction		Approximate Film Thickness (Å)
Temp. (°F)	Time (hr)	Reflection	Transmission	
820	1/6	$\text{FeO} \cdot \text{TiO}_2$	$\text{FeO} \cdot \text{TiO}_2$	300
820	1/2	$\text{FeO} \cdot \text{TiO}_2$	$\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot \text{TiO}_2$	500
1800	1/2	$\text{FeO} \cdot \text{Al}_2\text{O}_3$ (Possible $\text{FeO} \cdot \text{TiO}_3$)	Not identified	1500
1800	2	$\text{FeO} \cdot \text{Al}_2\text{O}_3$	Not identified	1500
1800	4	Al_2O_3	$\text{FeO} \cdot \text{Al}_2\text{O}_3$	2000

Another factor, apparent from Table 2, which may complicate the fabrication of dispersion-hardened alloys from oxidized base-alloy powders is that chemically active minor additions tend to appear in considerable concentration in the oxide, and the matrix is thereby depleted. As an indication of the extent to which this may happen, the free energies of formation of some of the oxides of the metals that may be present in the base alloy are listed:⁵¹

⁵¹F. D. Richardson and J. H. E. Jeffes, J. Iron Steel Inst. 160, 261 (1948).

<u>Compound</u>	<u>Free Energy of Formation kcal/mole at 1832°F</u>
Al_2O_3	- 303
Cr_2O_3	- 187
TiO_2	- 160
FeO	- 87

An indication of the inert nature of the oxide formed on this alloy was given by the fact that a typical surface film was not affected by a three-hour exposure to dry hydrogen (-74°F dew point) at 1600°F; no weight change occurred, and its color was unaltered.

It would appear from the above that an oxide consisting principally of Al_2O_3 can be grown on both binary Fe-Al and ternary Fe-Al-Cr alloys.

QUANTITATIVE FACTORS IN ALLOY DESIGN

It has been brought out previously in this report that the mechanical properties of a dispersion-strengthened alloy are largely a function of the dispersion characteristics, and depend principally on the mean free path between the particles. The rational design and preparation of such alloys necessitates, therefore, that means be available to relate the geometry of the dispersion in an alloy to the metallurgical variables involved in its preparation.

To be brought out in this section of the report are mathematical expressions of the interdependence of morphological variables, and the connection of these variables with the alloy concentration in the base material, its mechanical preparation, and its heat treatment.

Morphological Interrelationships

It can be understood intuitively that interparticle spacing, second-phase volume concentration, and particle size and shape are not mutually independent variables.

Derivations of relationships between these quantities are included in the Appendix to this report. Basic to these derivations are relations published by Howard and Cohen⁵² and by Fullman.⁵³ The relationship between morphological variables for a dispersion of spherical particles can be shown to be as follows:

⁵²R. I. Howard and M. Cohen, "Quantitative Metallography by Point Counting and Lineal Analysis," Trans. Met. Soc. AIME 172, 413 (1947).

⁵³R. L. Fullman, "Measurement of Particle Sizes in Opaque Bodies," Trans. Met. Soc. AIME 197, 447 (1953).

$$\lambda = \frac{2d}{3} \left(\frac{1}{f} - 1 \right) \quad (7)$$

where

λ = interparticle mean free path,

d = particle diameter, and

f = second phase volume fraction.

In the case of a dispersion of randomly oriented platelet particles, either circular or rectangular in outline, the relationship is

$$\lambda = 2t \left(\frac{1}{f} - 1 \right) \quad (8)$$

where t is the platelet thickness, and the other variables the same as in Eq. 7.

In SAP-type alloys made from surface-oxidized powders, the platelet dispersion tends to be aligned in the direction of extrusion. For this nonrandom orientation, the variables are related in this fashion:

$$\lambda = t \left(\frac{1}{f} - 1 \right) \quad (9)$$

where the variables are the same as the ones defined previously.

The nature of Eqs. 7 and 8 is shown graphically on Fig. 2. An important conclusion that can be drawn from an examination of this figure is that particle sizes on the order of hundredths of microns must be attained to achieve the required interparticle spacings while holding the volume concentration of oxide to less than 10%.

Control of Morphological Variables

Particle shape can be controlled by the manner in which the aggregate is prepared. When an oxide, carbide, or nitride is brought into being as an intrinsic substance by reacting the base alloy, platelet particles are the result of surface reactions, while reactions made to occur internally usually cause the formation of at least quasi-spherical particles. In mechanically mixed aggregates, of course, dispersed-particle shapes can be selected at will, as can their size and concentration.

Particle size for an intrinsic compound is a function of the base material composition and the conditions of the reactions which brings the compound into being. In the case of oxide dispersants, temperature and time-at-temperature govern the particle size. The relation between these variables and particle size must be determined empirically.

Interparticle spacing has already been shown to be a function of particle size, shape, and concentration. It, as well as the other morphological variables, can be determined by tedious processes involving the detailed examination and measurement of photomicrographs of finished alloys.⁵³ As has been mentioned, however, it is desirable to be able to control the preparation of an alloy so that its interparticle spacing can be predicted with at least a fair degree of precision.

The calculation of interparticle spacing can be accomplished with the aid of Eqs. 7, 8, and 9 provided that volume fraction and particle size are known quantities. In the case of platelet dispersions produced by compacting and extruding surface-oxidized powders, volume fraction can be readily calculated by means of the following equation:

$$f = \frac{VA}{V - A(\delta - \nu)} \quad (10)$$

where

A = surface area of unoxidized powder, cm²/g,

V = net metallic volume in powder, cm³/g,

ν = volume of oxide formed per unit area on powder, cm³/cm², and

δ = penetration of metal during oxidation, cm.

The quantities A and V can be determined by routine laboratory methods. The variables ν and δ can be computed from experimental data and plotted, for a given alloy, as functions of temperature and time.

Suggested methods for evaluating ν and δ have been worked out for two experimental techniques. In one case, it is assumed that quantitative analysis of the oxide is feasible. In the other, it is assumed that the oxide is sufficiently inert so that it can be separated from the base metal by chemical dissolution techniques. In each case, it is taken for granted that the densities of both metals can be determined.

When the composition of the oxide is known, ν and δ can be calculated by means of these equations:

$$\nu = \left(\frac{\phi_m}{1 - \phi_m} + 1 \right) \frac{W_2 - W_1}{\rho_o A W_1}, \quad (11)$$

and

$$\delta = \frac{\Phi_m (W_2 - W_1)}{AW_1 \rho_m (1 - \Phi_m)}, \quad (12)$$

where

Φ_m = weight fraction of metal in oxide,

ρ_m = density of metal,

ρ_o = density of oxide,

W_1 = weight of powder sample before oxidation,

W_2 = weight of powder sample after oxidation,

and the other variables are as defined previously.

When dissolution techniques are possible, V and δ can be determined as follows:

$$V = \frac{W_3}{\rho_o AW_1}, \quad (13)$$

and

$$\delta = \frac{W_1 - W_2 + W_3}{AW_1 \rho_m}, \quad (14)$$

where

W_3 = weight of residue after dissolution,

ρ_o = density of oxide,

and the other variables have meanings already assigned.

In the preparation of dispersion-hardened materials by forming an intrinsic oxide in or on a base alloy, the composition of the starting material must be such that alloy concentration in the final matrix can be maintained after part of the addition has been transformed to oxide. An expression which can be used to calculate alloy requirements in weight percent is as follows:

$$\text{Required metal addition} = \left(\frac{f}{1-f} \right) \left(\frac{\rho_o}{\rho_m} \right) \left(\frac{\Phi_m}{1-\Phi_m} \right) + \text{metal in matrix.} \quad (15)$$

SUMMARY OF CONCLUSIONS

Incidental conclusions arrived at as a result of considering each of the areas covered by this report have been noted in preceding sections, and will not be repeated here. The over-all results of the study should, however, be summarized.

It is probable that the high-temperature mechanical properties of the oxidation-resistant Fe-Al-Cr alloys discussed in this report can be enhanced by

dispersion hardening. The effect of a dispersion is closely related to the mean free path between the particles, and it appears that an array of particles spaced on the order of two or three microns apart would impart the desired characteristics to the matrix alloy.

The nature of the alloy is such that its native oxide formed at temperatures above 1800°F consists mainly of Al_2O_3 ; the mechanical and chemical properties of this compound, together with the fact that intrinsic oxides seem to be desirable as dispersants, point to the probability that a native-oxide dispersion would be satisfactory.

Preparation methods for dispersion-hardened alloys have not been fully explored and are not discussed in this report. Tentatively, it would appear that a variation of the SAP process, involving the compaction and extrusion of surface-oxidized powders, would be successful. Mathematical methods appear to be applicable to the design of such platelet-type dispersions.

The principal problem likely to be encountered in the development of useful alloys will be that of maintaining reasonable room-temperature ductility. There is reason to hope, however, that tensile elongations on the order of 10% may be achieved with the 2-3 μ interparticle spacing mentioned above.

RECOMMENDATIONS

A detailed proposal describing a program involving the preparation and testing of dispersion-strengthened Fe-Al-Cr alloys would be premature. There are at least ten possible methods which can be used in fabricating dispersion-hardened alloys, and it is recommended that the probable results of each of them be examined before any experimental work is undertaken. It is suggested that the following factors be considered in evaluating these techniques:

1. The composition of the oxide produced;
2. The shape of the oxide particles;
3. The ease with which particle size and concentration can be controlled;
4. The homogeneity of the matrix in the finished material;
5. The suitability of the process for economical bulk production of the alloy; and
6. The possible occurrence of second-phase segregation, anisotropy in the final alloy, and other defects.

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APPENDIX

DERIVATION OF EQUATIONS RELATING MORPHOLOGICAL VARIABLES

General

According to DeLesse's law⁵² the volume fraction of a constituent in a continuous aggregate is equal to the fraction of a random line drawn through the aggregate that passes through the constituent. If a random line is passed through a structure consisting of particles embedded in a matrix, then

Line fraction occupied by matrix = volume fraction occupied by matrix

or

$$N_L \lambda = 1 - f \quad (A-1)$$

where

N_L = number of particles intersected per unit length of line,

λ = mean interparticle free path, and

f = volume fraction of dispersed phase.

The number of particles intersected per unit length of line is equal to the product of the number of particles per unit volume and the probability of the line passing through any given particle:

$$N_L = N_v P \quad (A-2)$$

where

N_v = number of particles per unit volume, and

P = probability of the line intersecting a given particle.

Equations A-1 and A-2 can be combined and solved for the interparticle spacing, giving

$$\lambda = \frac{1 - f}{N_v P} \quad (A-3)$$

Spherical Particles

In the case of spherical particles, the volume fraction occupied by the second phase is, by definition

$$f = N_v \cdot \frac{4}{3} \pi r^3 \quad (A-4)$$

where r = particle radius.

This can be solved to give

$$N_v = \frac{3f}{4\pi r^3} \quad (A-5)$$

For spherical particles, the probability of a random line hitting a given particle is equal to the size of the particle, the target area it presents, so

$$P = \pi r^2. \quad (A-6)$$

Substituting Eqs. A-5 and A-6 into Eq. A-3, we obtain⁵³

$$\lambda = \frac{4r}{3} \left(\frac{1}{f} - 1 \right). \quad (A-7)$$

In terms of particle diameter, d,

$$\lambda = \frac{2d}{3} \left(\frac{1}{f} - 1 \right). \quad (7)$$

Platelet Particles

The volume fraction occupied by material in the form of circular platelet particles is

$$f = N_v \pi r^2 t, \quad (A-8)$$

and

$$N_v = \frac{f}{\pi r^2 t}, \quad (A-9)$$

where

t = platelet thickness, and

r = platelet radius.

The probability of a random line hitting a given randomly oriented platelet is equal to the average target area presented by a platelet. If $r \gg t$, as is usually the case,

$$P = \frac{1}{2} \pi r^2. \quad (A-10)$$

Substituting Eqs. A-9 and A-10 into Eq. A-3, we obtain

$$\lambda = 2t \left(\frac{1}{f} - 1 \right). \quad (8)$$

The derivation of similar expressions for dispersions having other characteristics is easily accomplished.

DERIVATION OF EQUATION FOR VOLUME FRACTION OF OXIDE FORMED BY SURFACE OXIDATION OF POWDERS

By definition,

$$f = \frac{\text{Volume of oxide formed}}{\text{Final volume of metal + volume of oxide formed}} \quad (\text{A-11})$$

The volume of oxide formed is

$$\text{Volume oxide} = VA \quad (\text{A-12})$$

where

V = volume of oxide formed per unit area on powder, cm^3/cm^2 , and
 A = surface area of unoxidized powder, cm^2/g .

The final volume of the metal is

$$\text{Final volume} = V - A\delta \quad (\text{A-13})$$

where

V = net metal volume in powder, cm^3/g , and

δ = penetration of metal during oxidation, cm.

Substituting Eqs. A-12 and A-13 into Eq. A-11 and simplifying, we obtain

$$f = \frac{VA}{V - A(\delta - V)} \quad (10)$$

DERIVATION OF EXPRESSIONS FOR δ AND V FOR USE WHEN OXIDE COMPOSITION IS KNOWN

a. If it can be assumed that the weight gained by a sample during the oxidation process is all oxygen, then the metal weight loss sustained by the sample will be

$$\text{Metal loss} = \frac{\phi_m(W_2 - W_1)}{1 - \phi_m} \quad (\text{A-14})$$

where

ϕ_m = weight fraction of metal in oxide,

W_1 = weight of powder sample before oxidation, g, and

W_2 = weight of powder sample after oxidation, g.

The metal loss is also equal to

$$\text{Metal loss} = \delta AW_1 \rho_m \quad (\text{A-15})$$

where ρ_m = metal density, and the other factors have been defined already.

Equating Eqs. A-14 and A-15 and solving for δ , we obtain

$$\delta = \frac{\Phi_m (W_2 - W_1)}{AW_1 \rho_m (1 - \Phi_m)} \quad (12)$$

b. If the density of the oxide can be determined or closely estimated, the volume of oxide formed on a powder sample can be readily calculated;

$$\text{Volume of oxide} = \frac{\text{Metal loss} + (W_2 - W_1)}{\rho_o} \quad (\text{A-16})$$

where ρ_o = oxide density, and the other variables have been defined previously.

The original surface area of the sample is AW_1 , so the volume of oxide formed per unit area of powder surface can be determined by combining this fact with Eqs. A-14 and A-16:

$$\nu = \left(\frac{\Phi_m}{1 - \Phi_m} + 1 \right) \frac{W_2 - W_1}{\rho_o AW_1} \quad (11)$$

DERIVATION OF EXPRESSIONS FOR δ AND ν FOR USE WHEN THE ACTUAL WEIGHT OF OXIDE FORMED ON A SAMPLE OF POWDER IS KNOWN AS A RESULT OF DISSOLUTION OF THE METAL

a. The volume of oxide formed per unit area on the powder can easily be seen to be

$$\nu = \frac{W_3}{\rho_o AW_1} \quad (13)$$

where W_3 = weight of residue remaining after dissolution treatment of the oxidized powder (assumed to equal the weight of oxide formed), and the other variables have already been defined.

b. The penetration of the metal resulting from the oxidation process can be calculated from weight data as follows:

The metal lost by the powder has been determined to be

$$\text{Metal loss} = \delta AW_1 \rho_m \quad (\text{A-15})$$

It can also be calculated as follows:

$$\begin{aligned} \text{Metal loss} &= \text{Original sample weight} - \text{weight of metal dissolved} \\ &= W_1 - (W_2 - W_3). \end{aligned} \quad (\text{A-17})$$

Equating expressions A-15 and A-17 and solving for δ , we obtain

$$\delta = \frac{W_1 - W_2 + W_3}{AW_1 \rho_m}. \quad (14)$$

DERIVATION OF EXPRESSION ESTABLISHING NECESSARY ACTIVE-METAL CONTENT OF ALLOY POWDER
SO THAT ACTIVE-METAL SOLID-SOLUTION CONCENTRATION IN ALLOY CAN BE MAINTAINED
WHEN PART OF IT HAS BEEN TRANSFORMED TO OXIDE

In terms of weight fractions,

$$\text{Required metal addition} = \text{Metal in oxide} + \text{metal in matrix.} \quad (\text{A-18})$$

An expression for the metal in the oxide can be written as follows:

$$\begin{aligned} \text{Metal in oxide} &= \left[f \frac{\text{cm}^3 \text{ oxide}}{\text{cm}^3 (\text{oxide} + \text{matrix})} \right] \left[\frac{1}{1 - f} \frac{\text{cm}^3 (\text{oxide} + \text{matrix})}{\text{cm}^3 \text{ matrix}} \right] \\ &\times \left[\frac{\rho_o \text{ g oxide}}{\text{cm}^3 \text{ oxide}} \right] \left[\frac{\text{cm}^3 \text{ matrix}}{\rho_m \text{ gm matrix}} \right] \left[\frac{\Phi_m \text{ g matrix}}{(1 - \Phi_m) \text{ g oxide}} \right]. \end{aligned} \quad (\text{A-19})$$

Substituting Eq. A-19 in A-18, we obtain

$$\text{Required metal addition} = \left(\frac{f}{1 - f} \right) \left(\frac{\rho_o}{\rho_m} \right) \left(\frac{\Phi_m}{1 - \Phi_m} \right) + \text{metal in matrix.} \quad (15)$$

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