# Review
# High-strength, high-temperature intermetallic compounds

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Materials that are solid at high temperatures are in demand for high-temperature structural applications, and materials that have high values of strength-to-weight and stiffness-to-weight are desired for aircraft and space applications. Basic properties that are insensitive to processing history can be used to provide a preliminary ranking of single-phase substances. A compilation is presented of 293 intermetallic compounds (or metal–metalloid compounds) that melt at $T \geqslant 1500°$ C. By displaying the data by crystal structure on plots of $T_m$ against the specific gravity $\varrho$, candidates for optimum specific strength and specific stiffness can be recognized for materials that are likely to have similar plastic properties.

## 1. Introduction
The mechanical properties of intermetallic compounds received considerable interest through the 1960s, as evidenced by several compilations [1–3]. Recent activity is also brisk [4], with a special stimulation being supplied by aerospace demands for materials that are strong, stiff, and ductile at high temperatures [5, 6].

The opportunity that many workers see derives most directly from the twin properties that have been observed in certain structures (1) of yield strength that increases with temperature over a considerable range of temperature [7] and (2) of significant ductility [8]. Ductility is found even in polycrystalline samples, provided composition is controlled both as to stoichiometry and as to solute additions, for example boron in the case of $Ni_3Al$, an $L1_2$ (cP4) structure [9]. Although the positive temperature variation of the flow stress has been observed most often in $L1_2$ structures [10], this behaviour is by no means specific to this structure, since it occurs in a $D2_b$ (tI26) compound [11] $Be_{12}Nb$, in the B2 (cP2) and $D0_3$ (cF16) compounds [12] FeCo and $Fe_3Al$, and an $L1_0$ (tP4) structure [13] TiAl. For FeCo and $Fe_3Al$ the effect occurs over temperatures where long-range order is decreasing, but decreasing order with temperature is not known to be present in the other cases just referenced. In short, some intermetallics have highly attractive elevated-temperature strengths and these materials are not restricted to a single anecdotal structure but occur in a significant variety of ordered compounds.

Other bonuses that many intermetallics offer are that their bonding is tighter than in the pure components of which they are formed, and hence they tend to have higher elastic stiffnesses and melting temperatures.

## 1.1. Obstacles and opportunities
The major hurdle in obtaining the required mechanical properties is the widespread tendency for intermetallics that have high melting temperatures to be brittle at ambient temperatures. Since intermetallic compounds may be thought of as being intermediate between metals and ceramics, the hope is to combine the best of each class, the ductility of metals and the strength and oxidation resistance of ceramics. It is recognized that often the reverse will happen: the low strength at high temperatures and easy oxidation of metals may associate with the brittleness of ceramics.

Because there is an immense diversity of crystal structure type and of individual compounds, only a small fraction of those that might be useful at elevated temperature have been tested. The aim in this review is to identify properties that will help to recognize what compounds are candidates for further study. For this initial purpose we wish basic, "structure-insensitive" properties that are not strongly dependent on processing history and the resultant microstructures. After identifying such properties, we present data for all the binary metallic compounds (or metal-metalloid compounds) that melt above 1500° C. These data will be identified and subdivided by crystal structure.

## 2. Selection of relevant basic properties
The basic properties of compounds that are compiled here are melting temperature $T_m$, specific gravity $\varrho$, and elastic modulus $E$ (Young's modulus), quantities that were emphasized earlier [14].

## 2.1. Melting temperature
For multiple reasons $T_m$ is by far the most useful structure-insensitive property:

(a) It specifies the thermal interval where materials are solid.

(b) Its relative magnitude is a reasonable first approximation to the stiffness of a material, since the elastic moduli have a strong correlation with melting temperature [15].

(c) In all models of strengthening, values of flow stress increase with the magnitude of the elastic constants, which in turn increase with $T_m$.

(d) Expansion coefficients (which for convenience should be small) vary inversely with $T_m$.

(e) The limiting creep rate defines a maximum operating temperature that increases with $T_m$. Approximate limits set on operating temperatures for single-phase materials are estimated to lie between $T_m/2$ and $2T_m/3$, with $T_m/2$ being more common [16]. A simple zero-order rule-of-thumb is that, if the melting temperature is expressed in degrees centigrade, the operating temperature is roughly the same number in degrees Fahrenheit. In short, a material that melts at 3400° C might be engineered to operate at 3400° F. Thus for five separate reasons, melting temperature is a figure of merit for material usefulness at high temperatures.

## 2.2. Specific gravity and elastic moduli

For use above the earth and in rotating parts, high specific strength (strength per unit density) and specific stiffness are important. It is, therefore, necessary to know the elastic moduli (as measures of stiffness and as structure-insensitive indicators of strength) and the specific gravity. Unfortunately, for intermetallic compounds there is a dearth of data on elastic moduli; measurements of $E$ were located for only 24 of $\sim 290$ intermetallics that melt at or above 1500° C. Although $E/\varrho$ is the specific stiffness (which we want to know) and the specific strength $\sigma/\varrho$ is roughly proportional to $E/\varrho$, we will in most cases be forced to reason more indirectly from $T_m/\varrho$ as roughly proportional to $E/\varrho$, and in turn still more roughly proportional to $\sigma/\varrho$.

## 3. Sources of data

Information was collected from a variety of standard sources [17–28] as well as from a number of miscellaneous articles that are too numerous to explicitly reference here. Included are previous lists of materials with high melting temperatures [14, 18] and standard collections of phase diagrams [19–23]. Since most of the specific gravities were not listed, they were therefore calculated from lattice parameters and crystal structures [19, 25, 26]. As noted earlier, for intermetallic compounds few elastic moduli are known; many of those used were from a collection of single-crystal data [27] and a reference periodical that includes moduli [28]. Computer searches located additional data.

## 4. Data

Overall distributions are considered first, followed by more detailed structure-by-structure data.

### 4.1. Numbers of compounds

Fig. 1 shows the locations on a specific gravity against melting-temperature diagram of the 293 binary compounds that melt at $\geqslant 1500°$ C. (The specific curve is
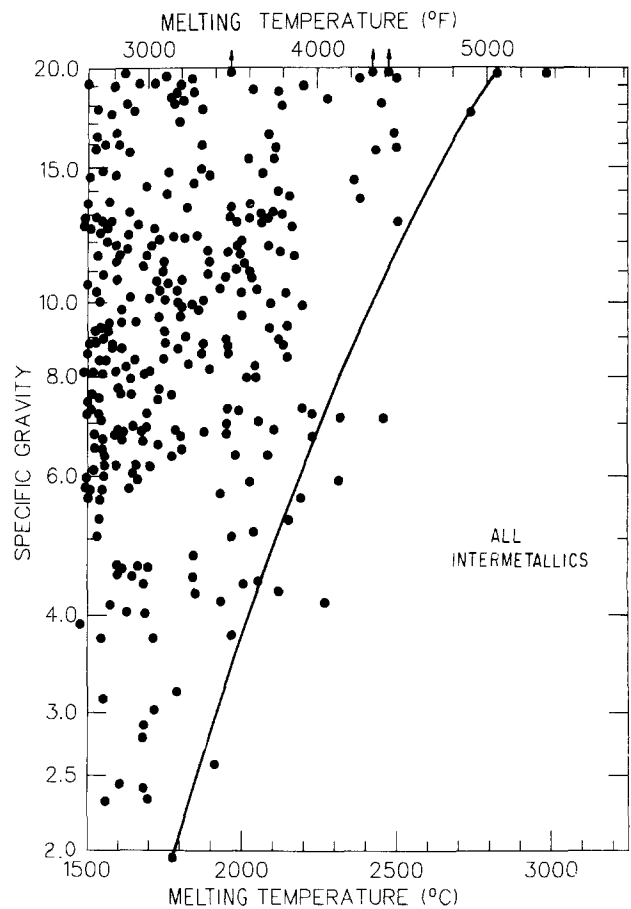


Figure 1 $T_m$ against $\varrho$ for the 293 binary intermetallic compounds surveyed. The solid line is an empirical, approximate envelope to the data.

an approximate envelope to the distribution; it will be discussed later.) Fig. 2 shows the distribution by density of the compounds, none with $\varrho < 1.5$ or $> 25$. Similarly Fig. 3 gives the number distribution with temperature, an exponential that drops above 1925° C (3500° F) by a factor of two for each 150° C (270° F). At lower temperature the slope is a factor of two for each 260° C (470° F), close to the 280° C (500° F) quoted earlier [14] for all binary compounds (i.e. not limited to intermetallics). In short, empirically the rapid decrease is general among high-temperature solids.
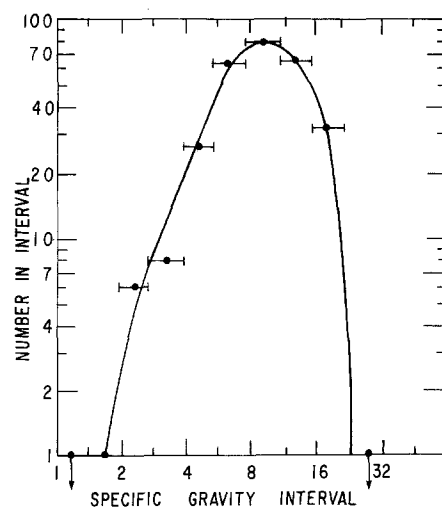


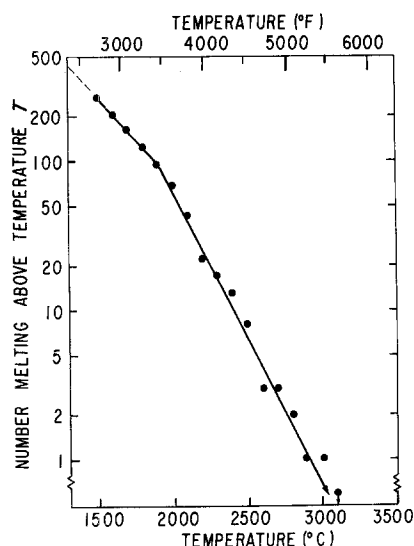Figure 2 Specific gravity distribution of the compounds.

Figure 3 Number of intermetallic compounds melting above a given temperature. The exponential decrease from 1500 to 2000° C is close to that seen [14] for all single element and binary compounds above 2000° C.

## 4.2. $T_m$ against $\varrho$ diagrams by crystal structure

Next we view $T_m$–$\varrho$ diagrams in which the individual compounds are identified and grouped by crystal structure (Figs 4 to 13). The structures are identified by Strukturbericht, type-compound, and Pearson designations in each diagram; the exception is Fig. 13, the key for which is given as Table I to avoid further crowding the figure.

It is evident that the various compounds of Figs 4 to 13 do not uniformly populate the occupied area in Fig. 1. In the discussion section we will note the significance of this observation in seeking materials for use at high temperatures.



Figure 4 $T_m$–$\varrho$ graph for B1 compounds.

TABLE I Structures and type-compounds for the "miscellaneous structures" graph (Fig. 13)

| Strukturbericht Name | Type | Pearson index |
|---|---|---|
| B3 | SZn | cF8 |
| $B_f^*$ | $\zeta$-BCr | oC8 |
| $B8_1$ | NiAs | hP4 |
| $B8_2$ | InNi$_2$ | hP6 |
| B19 | AuCd | oP4 |
| B20 | FeSi | cP8 |
| B27 | BFe | oP8 |
| B35 | CoSn | hP6 |
| C11$_b$ | MoSi$_2$ | tI6 |
| C16 | Al$_2$Cu | tI12 |
| C40 | CrSi$_2$ | hP9 |
| C49 | Si$_2$Zr | oC12 |
| D2$_d$ | CaCu$_5$ | hP6 |
| D5$_3$ | Mn$_2$O$_3$ | cI80 |
| D7$_3$ | P$_4$Th$_3$ | cI28 |
| D8$_2$ | Cu$_5$Zn$_8$ | cI52 |
| D8$_5$ | Fe$_7$W$_6$ | hR13 |
| D0$_e$ | Ni$_3$P | tI32 |
| E9$_3$ | CFe$_3$W$_3$ | cF112 |
| L6$_0$ | CuTi$_3$ | tP4 |
| | CeNi$_3$ | hP24 |
| | HgMn | tP2 |

*Also called B33.
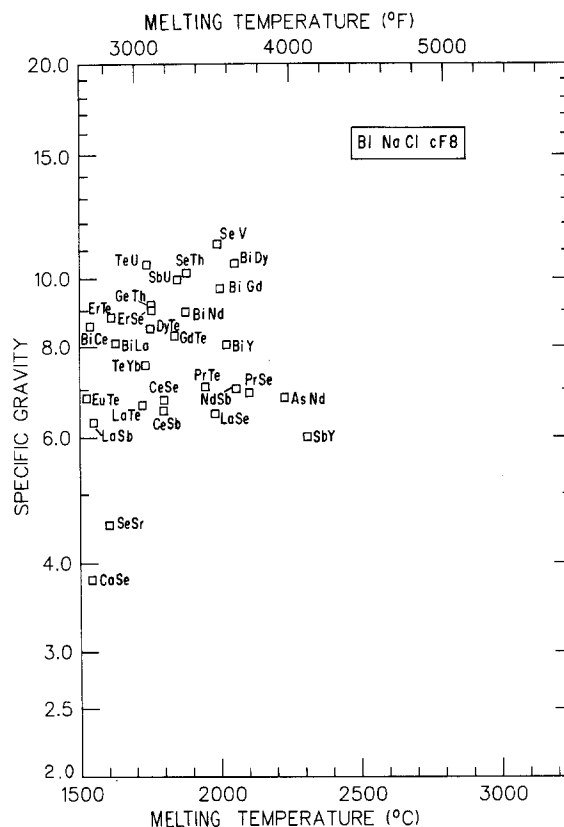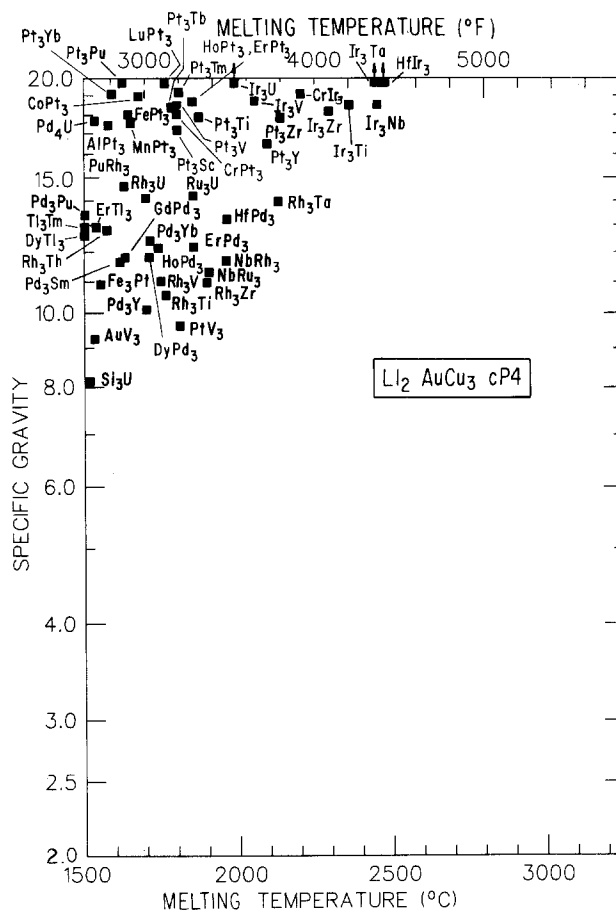


Figure 5 $T_m$–$\varrho$ graph for L1$_2$ compounds.

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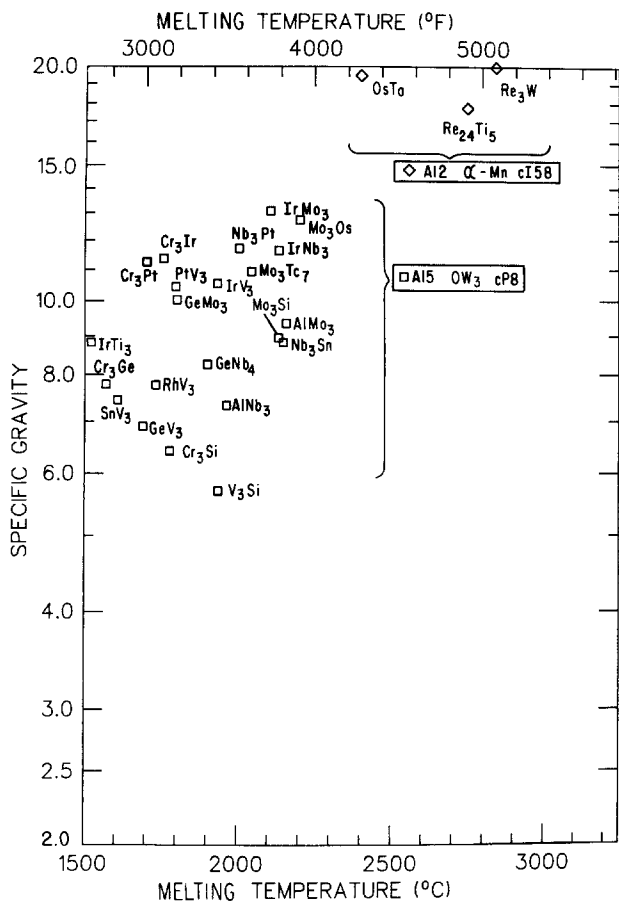
*Figure 6* $T_m-\varrho$ graph for A12 and A15 compounds.
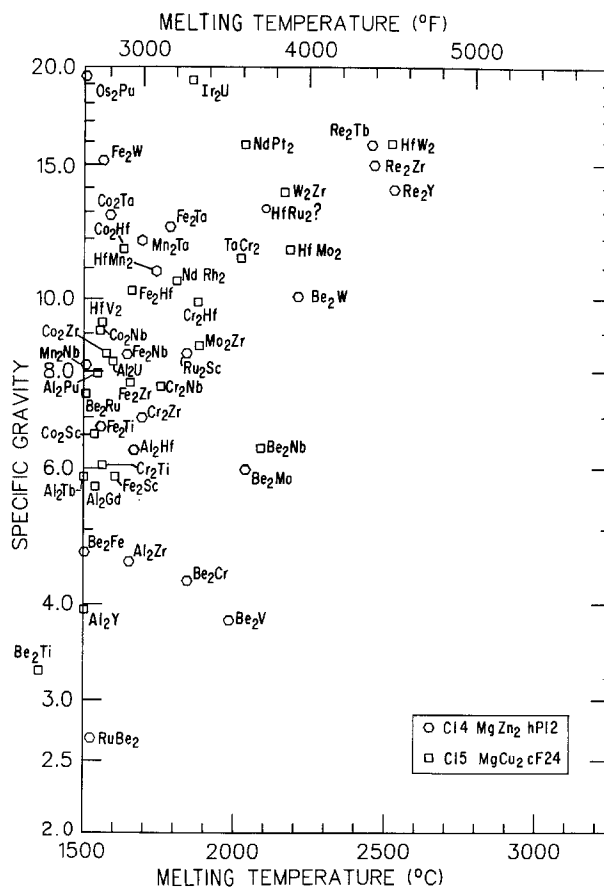


*Figure 8* $T_m-\varrho$ graph for C14 and C15 Laves phases.
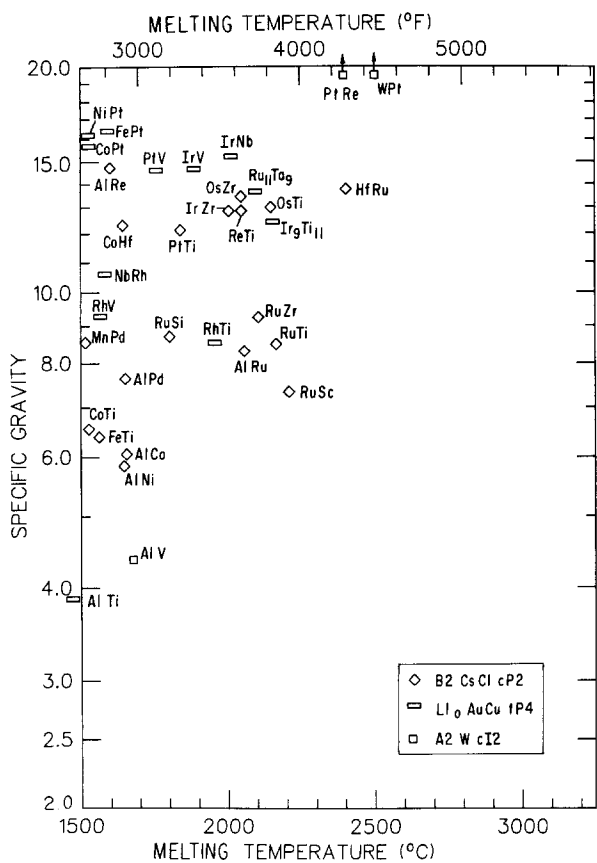


*Figure 7* $T_m-\varrho$ graph for B2, L1$_0$ and A1 compounds.
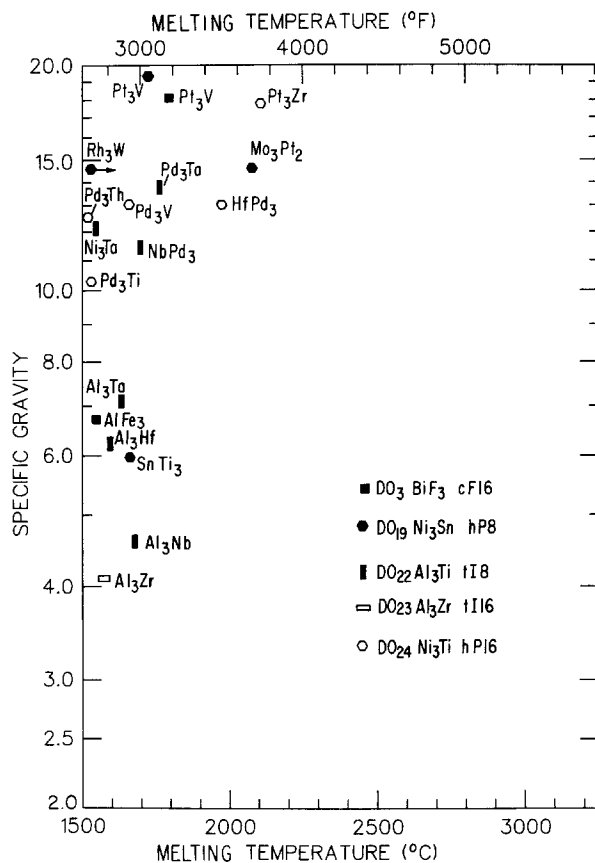


*Figure 9* $T_m-\varrho$ for various AB$_3$ compounds.
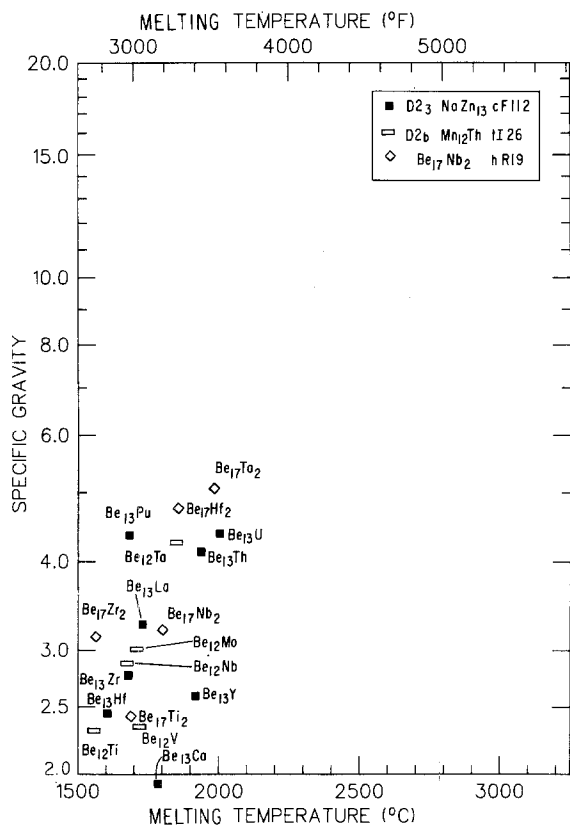
Figure 10 $T_m$-$\varrho$ for $A_{17}B_2$, $AB_{12}$ and $AB_{13}$ compounds.



Figure 12 $T_m$-$\varrho$ for D8$_b$ (sigma) phases.

## 4.3. $E/\varrho$ against $T_m$ data

As Fig. 14 shows, the data that include information on elastic moduli can be summarized more tersely than for $T_m$ against $\varrho$. Only 24 values of $E$ are available.

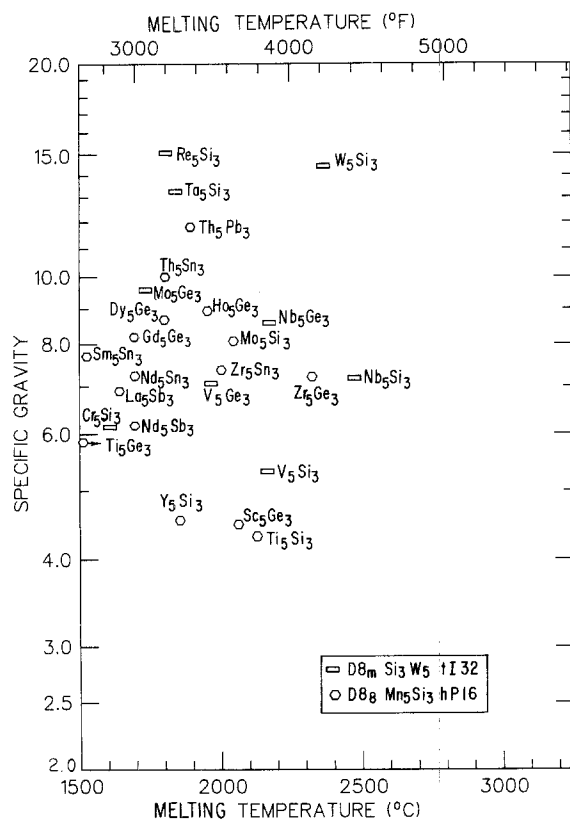## 5. Discussion

Here we first describe possible uses of the data
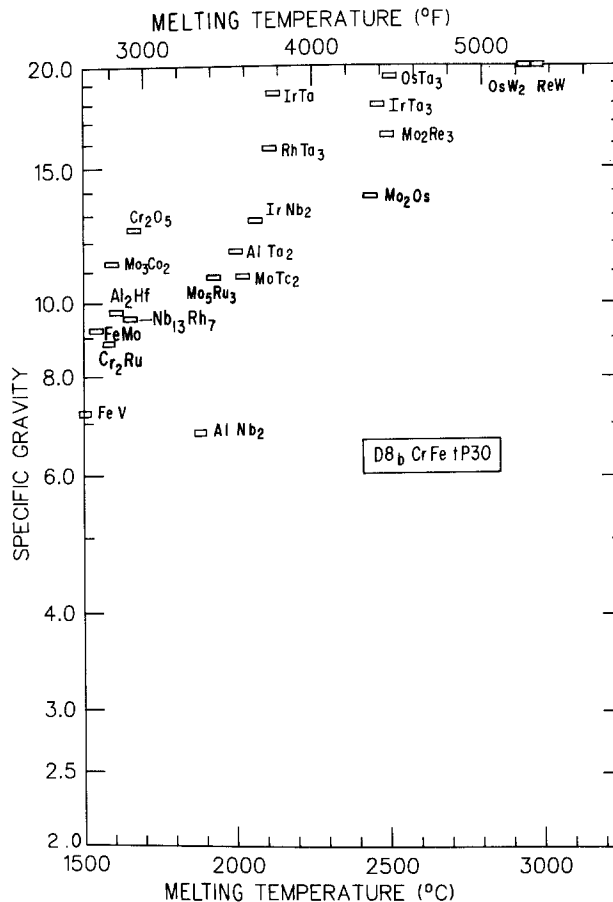


Figure 11 $T_m$-$\varrho$ for $A_5B_3$ Nowotny compounds.

presented and then consider the implications of the systematics.

## 5.1. Uses of $\varrho$-$T_m$ and $E/\varrho$-$T_m$ diagrams

From the proposed use of a mechanical part, criteria must be decided as to whether strength, stiffness, specific strength, specific stiffness, volume per unit strength, or something else is of greatest importance. With that information, diagrams such as Figs 4 to 14 can be used for preliminary ranking of materials. For example if solely strength is of importance, the materials with the highest $T_m$ values of Figs 4 to 13 would be considered first.

Aerospace applications: as noted earlier, there is major interest in strong, lightweight materials that can be used at elevated temperatures. For such applications both high $T_m$ (i.e. high strength and stiffness) and low $\varrho$ are desired. The most promising materials from the present point of view lie towards the lower right in Figs 1 and 4 through 13 and the upper right in Fig. 14. If a quantitative decision can be made as to the relative advantage of reducing $\varrho$ (and hence the weight that must be lifted) against increasing $T_m$ (and hence the maximum operating temperature and therefore the efficiency of an engine), then a set of parallel lines could be ruled on the figures (sloped upper right to lower left on Figs 1 and 4 through 13, and sloped in the opposite sense on Fig. 14). These lines then allow quantitative ranking of materials. We now consider quantitative values for the slopes of such lines, again considering the case of aircraft engines to provide a specific example.
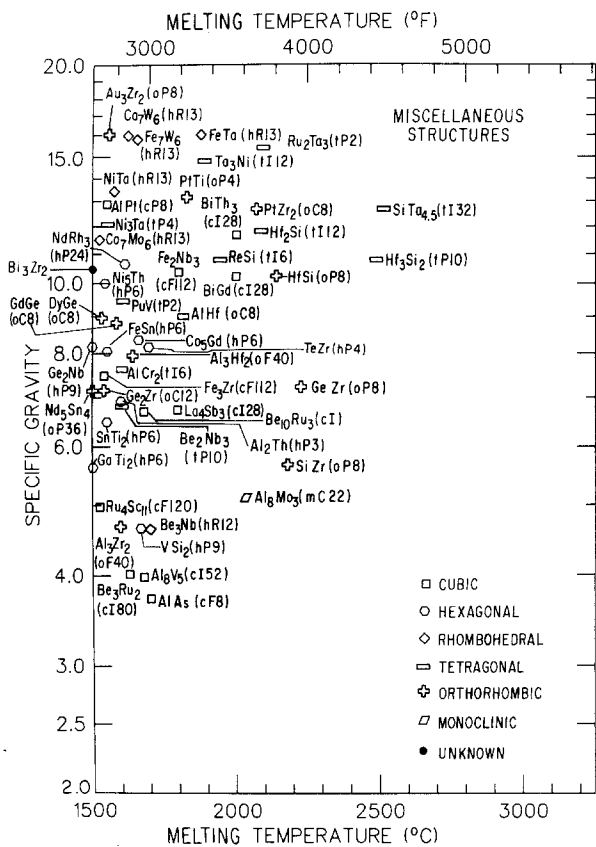
Figure 13 $T_m$–$\varrho$ for miscellaneous structures. See Table I for additional information.



Figure 14 $E/\varrho$ against $T_m$ for compounds for which Young's modulus ($E$) is known.

Aircraft engine parts, densities against operating temperature: generally if a material in an aircraft engine part can be replaced by a substance of lesser weight, either the performance is improved or extra useful weight can be added. Therefore, for each temperature requirement the lowest density material should be sought.

An exception to that rule applies to designing higher performance engines, since the maximum temperature sets a limit on the available thrust ($F$). If a new material, used in only a weight fraction of $f_p$ of the engine, allows a higher temperature to be reached, it can have a very powerful effect toward enhancing the overall thrust-to-weight ratio for the aircraft, even though the density of a particular part may be higher. If $dF/dT$ is the change in thrust with temperature, $W_A$ the weight of the aircraft, $f_e$ the fraction of $W_A$ taken up by the engines, and $\Delta\varrho$ the increase in specific gravity that accompanies a given increase in operating temperature $\Delta T$, then as long as

$$\frac{\Delta T}{\Delta\varrho}\frac{dF}{dT} > f_e f_p W_A \qquad (1)$$

the substitution is favourable. This applies to non-rotating parts.

We have arrived at two estimates of the benefits and rather different definite values. For example using the relation for the maximum $T_m$ envelope in Fig. 1, replacing a $\varrho = 8$ material with a $\varrho = 12$ one, should allow a 200° F (111° C) increase in operating temperature. For Mach 2 flight with a 4 : 1 compression ratio, an increase in thrust of about 20% is expected [29], which for a modern 1800 kg (40 000 lb) high-perform-
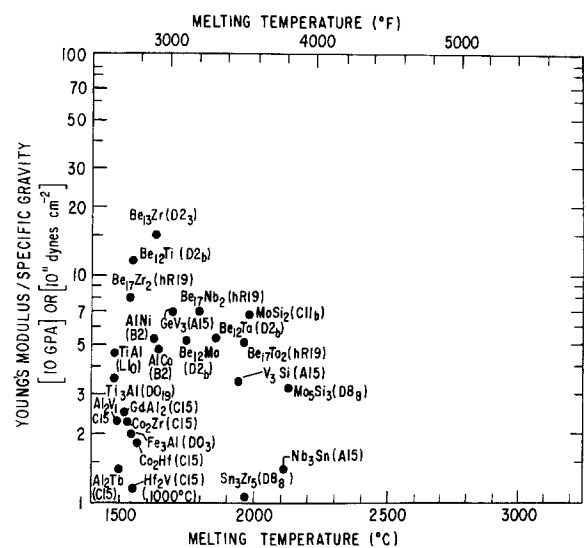
ance aircraft would be $\sim 3600$ kg ($\sim 8000$ lb). The cost in weight $W_A f_e f_p$ is roughly [(40 000)(0.12)(0.15) =] 720 lb (325 kg). For higher compression ratios up to 10 : 1 the benefits are still greater.

On the other hand for the F404-GE-400 turbofan engines used in the F18 fighter (gross weight of 51 900 lb = 2355 kg) the two engines each have 16 000 lb (7260 kg) thrust and a 25 : 1 compression ratio at Mach 1.85. For these conditions benefit in thrust for a 200° F increase is reported to be only 3% [30]. The gain in thrust is 960 lb (435 kg). The cost in weight for the same assumption (15% of the engine weight increased by 50%) is [2167(0.15)(2)(0.50) =] 320 lb (145 kg).

For rotating parts the merits of such a substitution are less decisive, since stresses are proportional to density for centripetal acceleration. The result is that to compensate for the added stress the temperature needs to be lowered to a temperature where that stress is tolerable. The net temperature change is positive only if

$$\left[\frac{d\sigma}{dT}\right] > \frac{\sigma}{\varrho}\left(\frac{\Delta\varrho}{\Delta T}\right),$$

where $d\sigma/dT$ is the decrease of stress with temperature at the particular stress $\sigma$ and strain rate that are of interest. The result is favourable in some cases and not in others; it must be evaluated individually.

Potential of intermetallic compounds: the envelope drawn in Fig. 1 can be used as a figure of merit for intermetallic compounds. Since few compounds appear to the lower right of the envelope, the closeness to the line may indicate the lightest, highest-strength intermetallic materials that are available.

## 5.2. Systematics

Effects of crystal structure: the different structures do not randomly populate the distribution of compounds shown in Fig. 1. Just as we could draw a rough envelope for the distribution in Fig. 1, we might draw analogous envelopes to describe the limits of the distributions for other crystal structures. Fig. 15
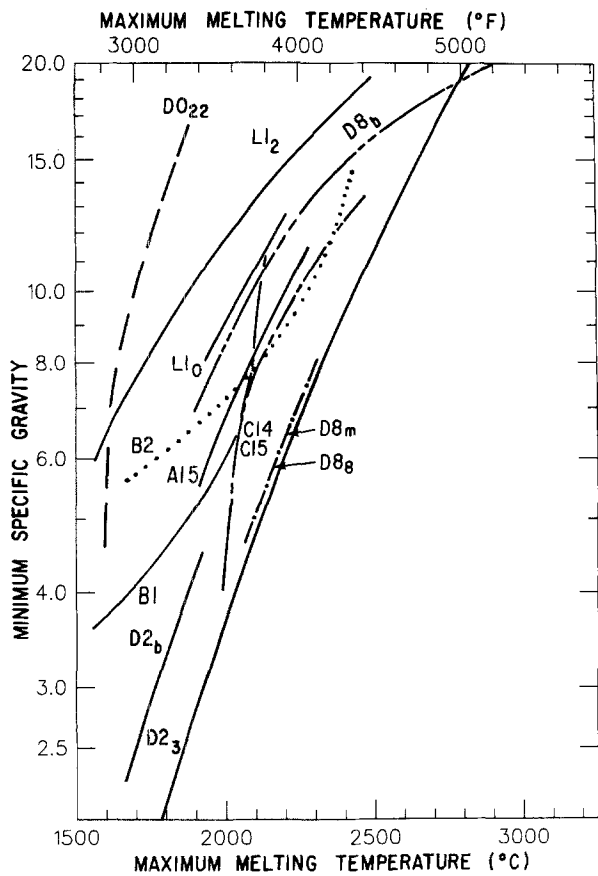
MAXIMUM MELTING TEMPERATURE (°F)
3000    4000    5000



Figure 15 Low ϱ-high $T_m$ envelopes for intermetallic compounds of different crystal structures.

allows such limits to be intercompared. The $L1_2$ structures, where the best success has been attained in obtaining both high-temperature strength and ambient-temperature ductility [7–9], lie to the left of the overall envelope, thus discouraging the idea that useful $Ni_3Al$ type behaviour might be directly extended to much higher temperatures merely by selecting other $L1_2$ compounds. Other structures may be needed to optimize properties at high temperature.

Is there a basic high-temperature limit? The existence of the rough limit to the data in Fig. 1 raises the question as to whether some fundamental law limits melting temperature for given compositions and struc-
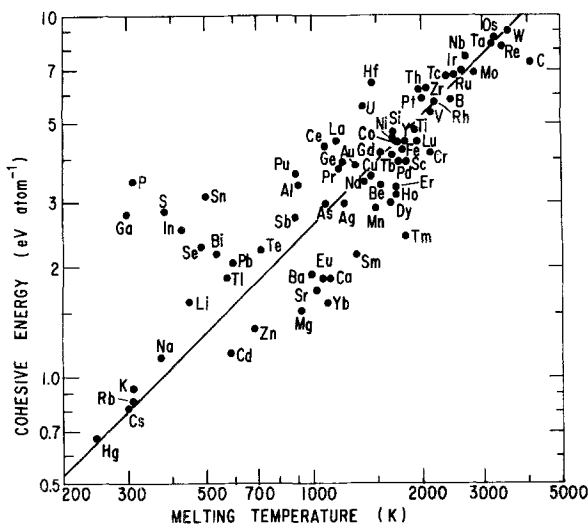
MAXIMUM MELTING TEMPERATURE (°F)
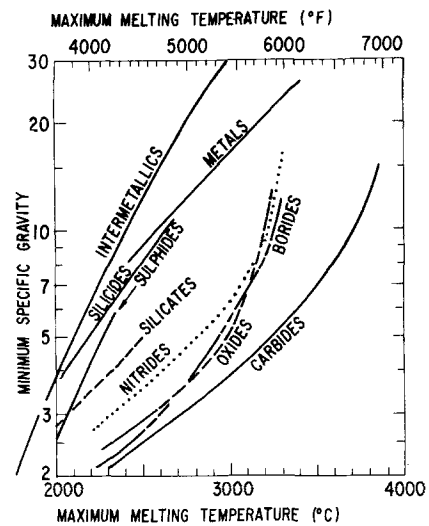4000    5000    6000    7000



Figure 17 Low ϱ-high $t_m$ envelopes for various binary compounds. Derived from a previous collection of data [14].

tures. Fig. 16 shows that in a crude sense the melting temperature may be taken as a measure of the cohesive energy of a solid, $E_c$. Thus the envelope given in Fig. 1 could be interpreted as a maximum value of $E_c$ that increases with the specific gravity of a material, i.e. with the electron density which binds the material together. This description is clearly rather qualitative and inexact; its purpose is to raise a question, rather than answer it.

Some added perspective may be derived from noting, as in Fig. 17, that the limits for other classes of solids, such as were considered earlier [14], are different both quantitatively and qualitatively.

## 6. Conclusions

Data on melting temperatures, specific gravities, and crystal structures have been compiled and presented, and descriptions and examples outlined as to how preliminary ranking of materials for various applications might be performed prior to material-by-material evaluation. In actual use many other considerations must be weighted and other properties be measured, many of them highly sensitive to processing history, microstructures, and alloying.

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Figure 16 Cohesive energy vs melting temperature for the elements.

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