

# Thermophysical Properties of L<sub>12</sub> Intermetallic Compounds of Iridium

## THERMAL CONDUCTIVITY AND THERMAL EXPANSION OF Ir<sub>3</sub>X FOR ULTRA HIGH-TEMPERATURE APPLICATIONS

By Yoshihiro Terada

Department of Materials, Physics and Energy Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan;

E-mail: terada@numse.nagoya-u.ac.jp

*Thermal conductivity and thermal expansion for the intermetallic compounds Ir<sub>3</sub>X (X = Ti, Zr, Hf, V, Nb or Ta) were measured in the temperature range between 300 and 1100 K. The thermal conductivities of Ir<sub>3</sub>X are distributed in the range from 41 to 99 W m<sup>-1</sup> K<sup>-1</sup> at 300 K, while the difference of thermal conductivities becomes less emphasised at higher temperatures. The coefficient of thermal expansion (CTE) values of Ir<sub>3</sub>X are insensitive to temperature, and fall around 8 × 10<sup>-6</sup> K<sup>-1</sup> at 800 K. The Ir<sub>3</sub>X intermetallic compounds with X = Ti, Zr, Hf, Nb or Ta are suitable for ultra high-temperature structural applications due to their higher thermal conductivities and smaller CTE values.*

The L<sub>12</sub> intermetallic compounds based on iridium (Ir<sub>3</sub>X) have been pursued as the next generation of high-temperature structural materials (1–6). The advantages of Ir<sub>3</sub>X are summarised as follows. Firstly, the melting points are between 600 and 1000 K higher than those of nickel-based superalloys (7). Secondly, an L<sub>12</sub> crystal structure offers the possibility of enhanced ductility as a result of the large number of possible slip systems. Finally, the two-phase  $\gamma/\gamma'$  type microstructure formed in Ni-based superalloys can also be produced in Ir-based alloys (8–10).

Thermal conductivity and thermal expansion are key parameters to evaluate the suitability of metallic materials for high-temperature structural applications (11, 12). Rapid heat transfer afforded by high thermal conductivity enables efficient cooling, which suppresses the appearance of life-limiting heat-attacked spots (6). A smaller thermal expansion is desirable to avoid thermal fatigue by cyclic thermal conditions, since thermal stress depends directly on the magnitude of the thermal expansion. However, no data on the thermal properties of Ir<sub>3</sub>X are available in the literature.

The Ir-based compounds Ir<sub>3</sub>X form an L<sub>12</sub> crystal structure when the partner component X belongs to Group 4 or 5 of the Periodic Table

(13–15). The present study was conducted to provide the data for thermal conductivity and thermal expansion of Ir<sub>3</sub>X (X = Ti, Zr, Hf, V, Nb or Ta) which serve to evaluate the suitability of the compounds for high-temperature structural applications. The alloy compositions prepared in this study are given in Table I, together with the compositional range of the L<sub>12</sub> phase at the homogenised temperature (1573 K) (7). The stoichiometric composition was chosen for each compound except Ir<sub>3</sub>Hf. Note that the composition close to stoichiometry with L<sub>12</sub> single phase was selected for Ir<sub>3</sub>Hf, since an L<sub>12</sub> single phase is not achieved at the stoichiometric composition.

Thermal conductivity measurements were performed by the laser flash method in vacuum in the temperature range between 300 and 1100 K, using a disc specimen of diameter 10 mm and thickness 2 mm (16). A short duration laser pulse is emitted from a ruby rod onto the surface of the disc specimen. The temperature change on the other side of the specimen was measured over time by both an infrared detector and a type R thermocouple. From the temperature-time profile, thermal conductivity was obtained (17). Thermal expansion measurements were made using a dilatometer

Table I

Chemical Composition of the  $\text{Ir}_3\text{X}$  Compounds Used in This Investigation, Together with the Composition Range of the  $\text{L1}_2$  Phase at the Homogenised Temperature (1573 K) (7)

Compound	Nominal composition, at.%	Composition range of $\text{L1}_2$ phase at 1573 K, at.%
$\text{Ir}_3\text{Ti}$	Ir-25.0Ti	23.6–26.7Ti
$\text{Ir}_3\text{Zr}$	Ir-25.0Zr	22.2–25.5Zr
$\text{Ir}_3\text{Hf}$	Ir-24.4Hf	23.5–24.5Hf
$\text{Ir}_3\text{V}$	Ir-25.0V	22.6–36.1V
$\text{Ir}_3\text{Nb}$	Ir-25.0Nb	24.0–32.0Nb
$\text{Ir}_3\text{Ta}$	Ir-25.0Ta	24.6–27.2Ta

which consists of an alumina pushrod driving a linear voltage differential transformer (LVDT) (18). Dilatometer specimens were normally 3 mm square and 8 mm long. Thermal expansion tests were conducted over the temperature range from 300 to 1100 K at a heating rate of  $10 \text{ K min}^{-1}$  in an argon atmosphere.

### Thermal Conductivity

Figure 1 shows the thermal conductivities of  $\text{Ir}_3\text{X}$  compounds as a function of temperature. The thermal conductivity tends to decrease with

increasing temperature for  $\text{Ir}_3\text{Nb}$  and  $\text{Ir}_3\text{Ta}$ , which have thermal conductivities above  $80 \text{ W m}^{-1} \text{ K}^{-1}$  at 300 K. Conversely, a continuous increase in thermal conductivity with increasing temperature is observed for  $\text{Ir}_3\text{V}$ , which has a smaller thermal conductivity at 300 K. The thermal conductivities of  $\text{Ir}_3\text{Ti}$ ,  $\text{Ir}_3\text{Zr}$  and  $\text{Ir}_3\text{Hf}$  are rather insensitive to temperature. The thermal conductivities of  $\text{Ir}_3\text{X}$  at 300 K are widely distributed in the range from 41 to  $99 \text{ W m}^{-1} \text{ K}^{-1}$ , while the difference becomes less emphasised at higher temperatures.

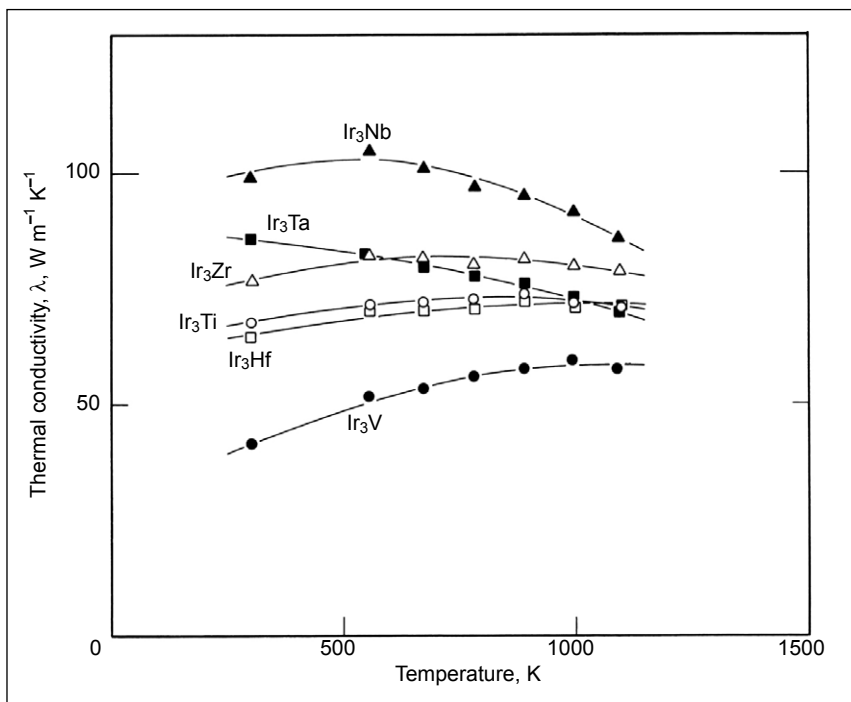


Fig. 1 Thermal conductivity versus temperature for  $\text{Ir}_3\text{X}$  ( $X = \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}$  or  $\text{Ta}$ ). Note that the value of  $\text{Ir}_3\text{Hf}$  is the off-stoichiometric data

The temperature coefficient of thermal conductivity,  $k$ , in the temperature range between 300 and 1100 K can be estimated from Equation (i):

$$k = (1/\lambda_{300\text{K}})(d\lambda/dT) \\ \approx (1/\lambda_{300\text{K}})\{(\lambda_{1100\text{K}} - \lambda_{300\text{K}})/(1100 - 300)\} \quad (i)$$

where  $\lambda_{300\text{K}}$  and  $\lambda_{1100\text{K}}$  are the thermal conductivities at the temperature indicated by the subscript. The temperature coefficients of  $\text{Ir}_3\text{X}$  are plotted against the thermal conductivity at 300 K in Figure 2, together with the plots for pure metals (19–21) and intermetallic compounds (22–24).

As a general rule, the thermal conductivity and the temperature coefficient are inversely correlated

in pure metals and intermetallic compounds. All the  $\text{Ir}_3\text{X}$  compounds other than  $\text{Ir}_3\text{V}$  are characterised by larger thermal conductivities and smaller temperature coefficients. In particular, the thermal conductivities of  $\text{Ir}_3\text{Nb}$  and  $\text{Ir}_3\text{Ta}$  are nearly equal to that of  $\text{NiAl}$ , which is widely recognised as a high thermal conductivity compound (17, 25).

The thermal conductivity of an intermetallic compound is quantitatively correlated with those of the constituents of the compound though Nordheim's relation (26). The high thermal conductivities of  $\text{Ir}_3\text{X}$  may be partly due to the high thermal conductivity of pure Ir, whose thermal conductivity at 300 K is  $147 \text{ W m}^{-1} \text{ K}^{-1}$ .

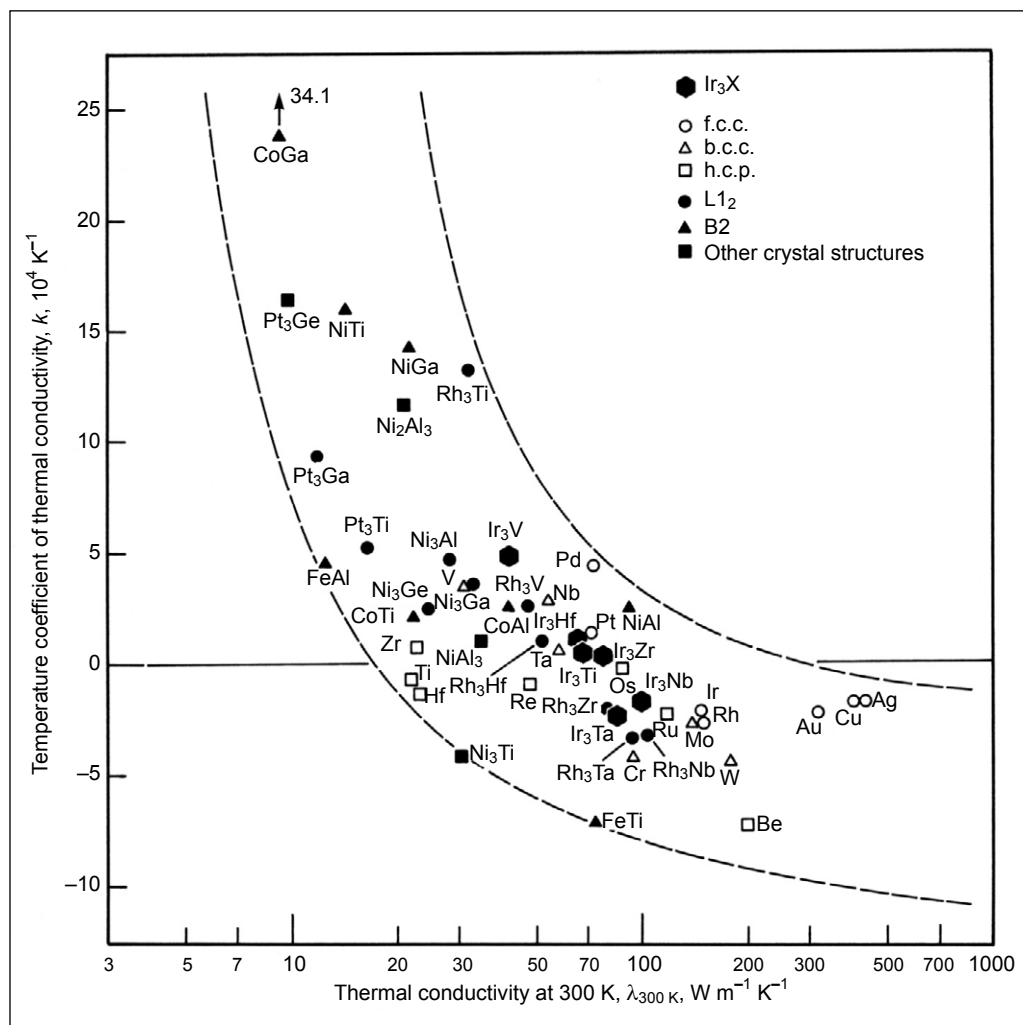


Fig. 2 Correlation between thermal conductivity at 300 K and temperature coefficient for  $\text{Ir}_3\text{X}$ . The data for pure metals (19–21) and intermetallic compounds (22–24) are also indicated

## Thermal Expansion

Results of the thermal expansion measurements ( $\Delta L/L$ ) are shown in Figure 3. The dilatation curves for all the  $\text{Ir}_3\text{X}$  compounds are smooth functions of temperature exhibiting no sudden changes in slope. The curves in Figure 3 reveal that the thermal expansion of  $\text{Ir}_3\text{Ta}$  is slightly smaller than that of either  $\text{Ir}_3\text{V}$  or  $\text{Ir}_3\text{Nb}$  over the temperature range between 300 and 1100 K. Also, the data indicate the smaller thermal expansion of  $\text{Ir}_3\text{Ti}$  in comparison with those of  $\text{Ir}_3\text{Zr}$  and  $\text{Ir}_3\text{Hf}$ .

The slope of the curve of  $\Delta L/L$  vs. temperature is the CTE. The relatively flat dilatation curve for each compound indicates that the CTE of  $\text{Ir}_3\text{X}$  are insensitive to temperature in the range 300 to 1100 K. The CTE of  $\text{Ir}_3\text{X}$  compounds at 800 K are summarised in Table II. All the values of CTE are concentrated around  $8 \times 10^{-6} \text{ K}^{-1}$ . The largest CTE is found in  $\text{Ir}_3\text{V}$  with  $8.4 \times 10^{-6} \text{ K}^{-1}$ , while  $\text{Ir}_3\text{Ti}$  shows the smallest at  $7.5 \times 10^{-6} \text{ K}^{-1}$ .

Figure 4 shows the correlation between the CTE at 800 K and the melting point for  $\text{Ir}_3\text{X}$ , together with the plots for pure metals (21, 27) and intermetallic compounds (22, 28). It is found that

Table II

Coefficient of Thermal Expansion of  $\text{Ir}_3\text{X}$  Compounds at 800 K

Compound	Coefficient of thermal expansion at 800 K, $\text{K}^{-1}$
$\text{Ir}_3\text{Ti}$	$7.5 \times 10^{-6}$
$\text{Ir}_3\text{Zr}$	$8.2 \times 10^{-6}$
$\text{Ir}_3\text{Hf}^*$	$8.2 \times 10^{-6}$
$\text{Ir}_3\text{V}$	$8.4 \times 10^{-6}$
$\text{Ir}_3\text{Nb}$	$8.0 \times 10^{-6}$
$\text{Ir}_3\text{Ta}$	$7.6 \times 10^{-6}$

\*Note that the value of  $\text{Ir}_3\text{Hf}$  is the off-stoichiometric data

all the plots of pure metals and intermetallic compounds including  $\text{Ir}_3\text{X}$  are arranged by a universal curve, irrespective of crystal structure. The CTE of  $\text{Ir}_3\text{X}$  are approximately equal to that of pure Ir and one half those of conventional intermetallic compounds such as  $\text{Ni}_3\text{Al}$  and  $\text{NiAl}$ . The smaller CTE values of  $\text{Ir}_3\text{X}$  correlate well with the higher melting points of the compounds.

The interatomic force in metallic materials is characterised by cohesive energy,  $E_{\text{coh}}$ , defined as the difference between the potential energy of atoms in the gas state and that in a crystal of the

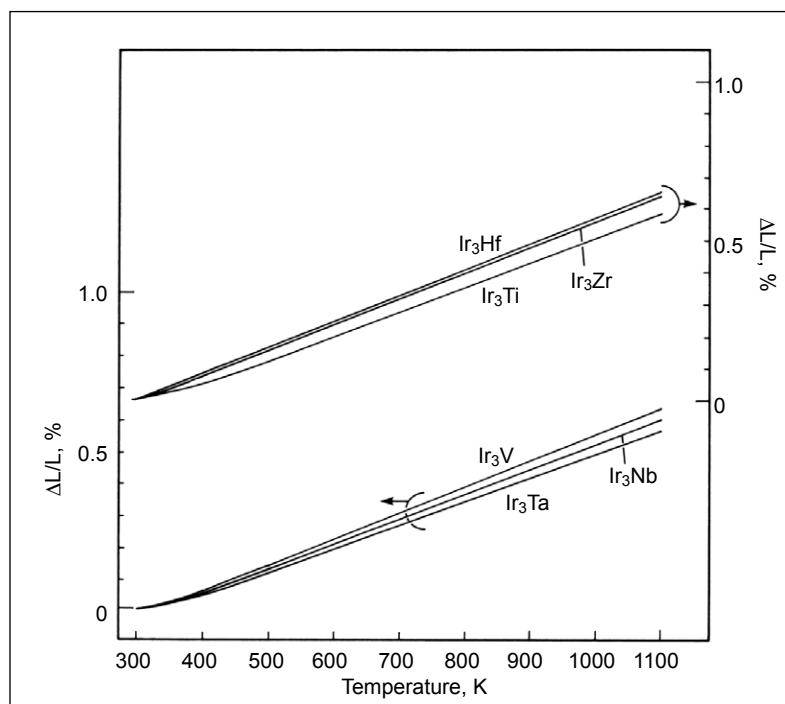


Fig. 3 Thermal expansion of  $\text{Ir}_3\text{X}$  during heating from 300 to 1100 K. The heating rate is  $10 \text{ K min}^{-1}$ . Note that the curve of  $\text{Ir}_3\text{Hf}$  is the off-stoichiometric data. Left-hand axis:  $\text{Ir}_3\text{V}$ ,  $\text{Ir}_3\text{Ta}$ ,  $\text{Ir}_3\text{Nb}$  Right-hand axis:  $\text{Ir}_3\text{Hf}$ ,  $\text{Ir}_3\text{Ti}$ ,  $\text{Ir}_3\text{Zr}$

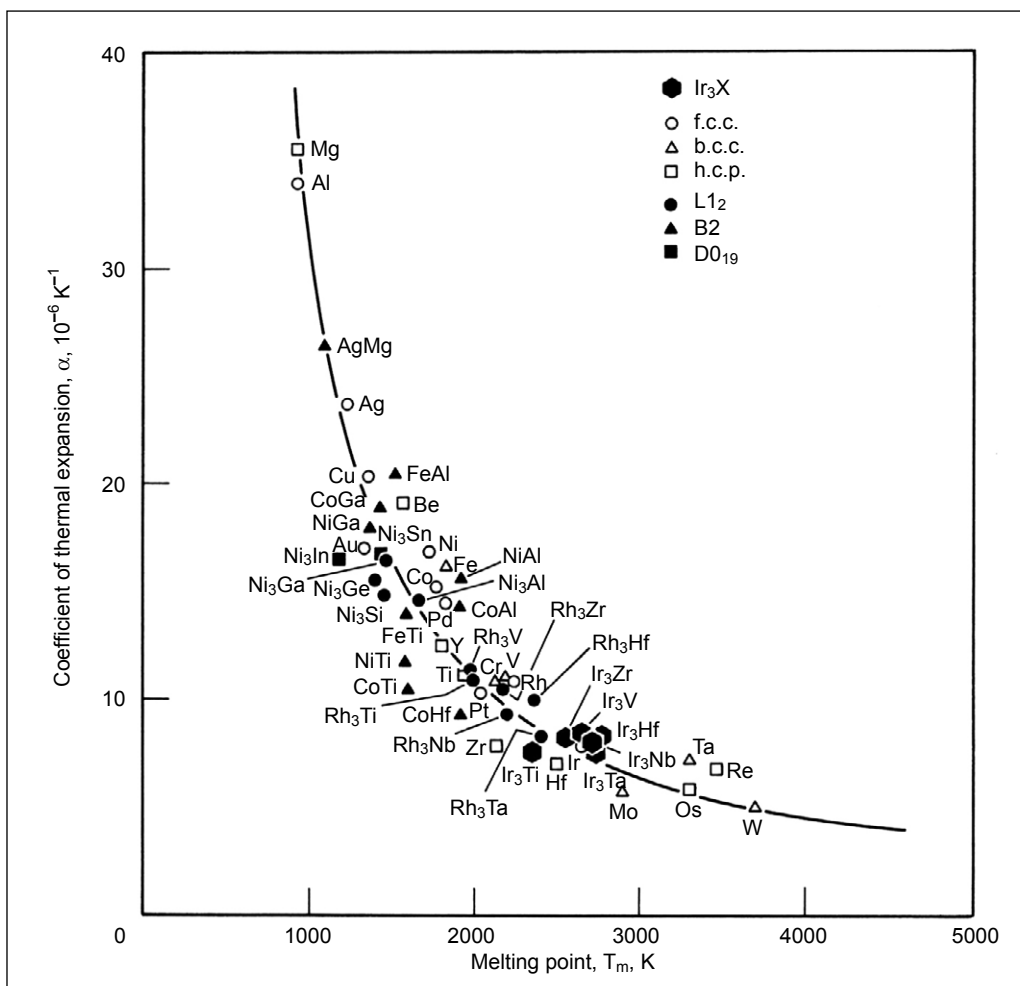


Fig. 4 Correlation between coefficient of thermal expansion at 800 K and melting point for  $\text{Ir}_3\text{X}$ . The data for pure metals (21, 27) and intermetallic compounds (22, 28) are also indicated

material. The cohesive energy in intermetallic compounds is expressed as the sum of the sublimation energy of the alloy,  $E_{\text{sub}}$ , and the heat of formation of ordered structure,  $\Delta H$  (29), Equation (ii):

$$E_{\text{coh}} = E_{\text{sub}} + \Delta H \quad (\text{ii})$$

Table III summarises the  $E_{\text{coh}}$ ,  $E_{\text{sub}}$  and  $\Delta H$  values for the  $\text{Ir}_3\text{X}$  compounds, where  $E_{\text{sub}}$  was obtained from the data source (30) and  $\Delta H$  was calculated from Miedema's formula (31, 32). The data for  $\text{Ni}_3\text{Al}$  and  $\text{NiAl}$  are also indicated in Table III. It can be seen that the cohesive energy of intermetallic compounds originates mostly from the sublimation energy rather than the heat of forma-

tion of ordered structure. The cohesive energy for  $\text{Ir}_3\text{X}$  is located around  $700 \text{ kJ mol}^{-1}$ , which is 1.7 times larger than that of  $\text{Ni}_3\text{Al}$  and  $\text{NiAl}$ . The larger cohesive energy of  $\text{Ir}_3\text{X}$  would result in the higher melting point and in the smaller CTE of the compounds.

## Conclusions

Thermal conductivity and thermal expansion of  $\text{Ir}_3\text{X}$  ( $\text{X} = \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}$  or  $\text{Ta}$ ) were surveyed in the temperature range between 300 and 1100 K. The thermal conductivity and the temperature coefficient are inversely correlated for  $\text{Ir}_3\text{X}$ . All the  $\text{Ir}_3\text{X}$  compounds other than  $\text{Ir}_3\text{V}$  have larger thermal conductivities and smaller temperature

Compound	Cohesive energy, $E_{\text{coh}}$ , kJ mol <sup>-1</sup>	Sublimation energy*, $E_{\text{sub}}$ , kJ mol <sup>-1</sup>	Heat of formation**, $\Delta H$ , kJ mol <sup>-1</sup>
Ir <sub>3</sub> Ti	675	620	55
Ir <sub>3</sub> Zr	732	653	79
Ir <sub>3</sub> Hf	728	658	70
Ir <sub>3</sub> V	662	631	31
Ir <sub>3</sub> Nb	737	685	52
Ir <sub>3</sub> Ta	749	698	51
Ni <sub>3</sub> Al	436	403	33
NiAl	426	378	48

\*Sublimation energy is obtained from the data source (30)

\*\*Heat of formation is calculated from Miedema's formula (31, 32)

coefficients. The CTE of Ir<sub>3</sub>X compounds are insensitive to temperature, and fall around  $8 \times 10^{-6}$  K<sup>-1</sup> at 800 K. The smaller CTE of Ir<sub>3</sub>X are well correlated with the higher melting points of the

compounds. The L1<sub>2</sub> intermetallic compounds Ir<sub>3</sub>X with X = Ti, Zr, Hf, Nb and Ta are characterised by larger thermal conductivity and smaller thermal expansion.

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**The Author**



Yoshihiro Terada is an Associate Professor in the Department of Materials, Physics and Energy Engineering, Nagoya University, Japan. His main activities are in the thermal and mechanical properties in metallic materials for high-temperature applications. His major field of present interest is the creep mechanisms of heat resistant magnesium alloys.