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Development of New Cryocooler Regenerator Materials – Ductile Intermetallic Compounds

K.A. Gschneidner, Jr.[1,2], A.O. Pecharsky[1], and V.K. Pecharsky[1,2]

[1]Materials and Engineering Physics Program, Ames Laboratory
Iowa State University, Ames, Iowa 50011-3020

[2]Department of Materials Science and Engineering
Iowa State University, Ames, Iowa 50011-2300, USA

ABSTRACT

The volumetric heat capacities of a number of binary and ternary Er- and Tm-based intermetallic compounds, which exhibited substantial ductilities, were measured from ~3 to ~350 K. They have the RM stoichiometry (where R = Er or Tm, and M is a main group or transition metal) and crystallize in the CsCl-type structure. The heat capacities of the Tm-based compounds are in general larger than the corresponding Er-based materials. Many of them have heat capacities which are significantly larger than those of the low temperature (<15 K) prototype cryocooler regenerator materials $HoCu_2$, Er_3Ni and ErNi. Utilization of the new materials as regenerators in the various cryocoolers should improve the performance of these refrigeration units for cooling below 15 K.

INTRODUCTION

Lanthanide materials have been used as low temperature (<20 K) regenerators since 1990 because of their large magnetic entropies at their magnetic ordering temperatures[1]. This development allowed Toshiba scientists[2,3] to reduce the low temperature limit of a two stage Gifford-McMahon cryocooler from 10 to 4 K by replacing some of the Pb with Er_3Ni in the low temperature stage regenerator. Since then, Nd[4] and $HoCu_2$[5] have been used as replacements for Er_3Ni; and the $Er_{1-x}Pr_x$ alloys ($0 \le x \le 0.50$) as a substitute for Pb[6,7] for cooling down to between 60 and 10 K. $GdAlO_3$ ($T_C = 3.8$ K) has been employed to cool to 4 K when utilized in the coldest section of a compound regenerator[8]. Below we discuss our latest work on the development of regenerator materials – ductile intermetallic compounds which have high volumetric heat capacities in the vicinity of the magnetic ordering temperatures between 4 and 16 K.

EXPERIMENTAL DETAILS

The alloys were prepared by arc-melting stoichiometric amounts of the component materials on a water cooled copper hearth under an argon atmosphere. The alloys were generally turned over 6 times (except for ErIr which was turned over ~20 times) and remelted to ensure a homogeneous ingot. Weight losses after melting were negligible. The metals used in this study were purchased from various commercial sources. The rare earth metals were 95 to 98 atomic percent pure with the major impurities being O, C and N, while the non-rare earth metals were 99.9+ atomic percent pure. The x-ray powder diffraction data were collected on an automated Scintag powder diffractometer using Cu K_α radiation to check on the phase purity and the crystallography of the samples. All of the samples were found to be single-phase materials within the limitations of the x-ray powder diffraction technique (typically 2 to 5 vol.% of an impurity phase). Most of the intermetallic compound samples were not heat treated because they were single phase alloys after arc-melting. ErRh and ErAu, however, were heat treated for 335 hours (2 weeks) at 900°C and rapidly quenched to room temperature to retain the B2 structure. The heat capacities at constant pressure were measured using an adiabatic heat-pulse-type calorimeter[9] from ~3.5 to ~350 K in zero magnetic field.

DUCTILE INTERMETALLIC COMPOUNDS

Magnetic lanthanide intermetallic compounds exhibit a wide range of magnetic ordering temperatures ranging from less than 1 K to nearly 1300 K. Of particular interest to the cryocooler industry are those compounds which order magnetically below 20 K[1]. Although many compounds have high heat capacities at the required temperature and thus would perform well as passive regenerator materials, their mechanical properties are far from ideal. In general, as most stoichiometric compounds, they are inherently brittle. Thus, they are nearly impossible to fabricate into sheets, jelly rolls, wires, and screens, which can be assembled into a regenerator which is more efficient than a packed bed of spheres. Furthermore, because of this brittleness the spheres can decrepitate and eventually leading to the failure of the regenerator and therefore the cryocooler. Thus, if one could make the brittle intermetallic compounds into ductile materials, or if one could find ductile intermetallic phases with suitable thermal properties, either development would be a major breakthrough in improving the efficiency of low temperature cryocoolers. Recently, we have discovered such a family of compounds which have unprecedented ductility (as high as 20%) and high fracture-toughness at room temperature[10]. This family of equiatomic compounds, RM, is made up of a rare earth (R) and a main group or transition metal (M) atoms, and has the B2, CsCl-type structure (see Fig. 1). There are over 120 known members in this family. Some of these binary RM phase have high heat capacities below 20 K [e.g. ErCu, $T_O \cong 8.5$ K and 13 K[11]; ErAg $T_O \cong 15.5$ K[12]; TmCu, $T_O \cong 6.5$ and 8 K[11,13]; and TmAg, $T_O \cong 7$ K[13] (the ordering temperatures listed here are those found in this study, which may differ slightly from earlier values reported in the literature)], and thus are of interest to the cryocooler community. Indeed, Biwa *et al.*[14] have proposed that ErAg be utilized as a

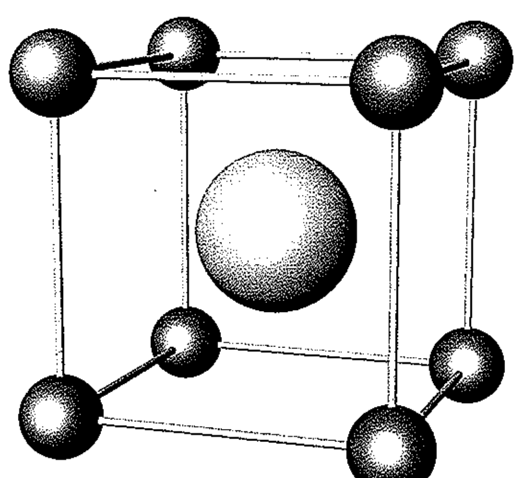

Figure 1. The B2 CsCl-type crystal structure. The larger sphere shown in the center of the unit cell represents the rare earth metal atom, while the smaller spheres on the corners represent the non-rare earth metal (a main group or a transition metal) atom.

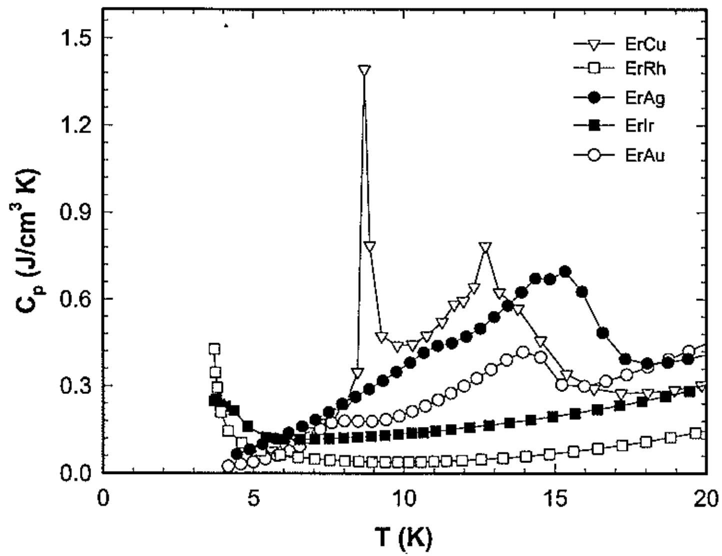

Figure 2. The volumetric heat capacities of ErCu, ErRh, ErAg, ErIr and ErAu from ~4 to 20 K.

regenerator material from 9 to 17 K, but they did not realize that this compound is a ductile intermetallic. In addition to their ductilities, these B2 compounds are stable in air and have good oxidation resistance at room temperature.

Alloying studies have been carried out on ErCu and TmCu to establish: (1) whether the two ordering peaks can be merged or shifted closer together to design an alloy which would have a larger heat capacity over a broader temperature range, and thus may increase the efficiency of the regenerator; and (2) how much the major heat capacity peak temperature (the lower ordering one) could be shifted upward or downward to give some flexibility in designing regenerators to fit a particular requirement.

RESULTS AND DISCUSSION

The pure B2 RM binary compounds studied include ErCu, ErRh, ErAg, ErIr, ErAu, TmCu and TmAg. In addition, many ternary R(M,M′) and (R,R′)M compounds were studied, especially the ErCu- and TmCu-base materials. The non-rare earth dopants include Al, Mn, Fe, Ni, Co, Zn, Ga, Ru and Ag, while the rare earth additives were Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm and Lu.

Binary B2 RM Compounds

The volumetric heat capacities of the binary ErM (where M = Cu, Rh, Ag, Ir, Au) B2, CsCl-type intermetallic compounds are shown in Fig. 2. Of these five compounds, only ErCu has two magnetic ordering temperatures (~8.5 and ~12.7 K), while the others probably have one magnetic transition: ErAg at about 16 K, ErAu at about 14 K, and ErRh and ErIr below 4 K. It is possible that ErAu may have a second magnetic transition at about 7.5 K but this needs to be verified by other physical property measurements such as the magnetic susceptibility or electrical resistivity. The upswing in the volumetric heat capacity below 5 K of ErRh and ErIr suggests that these two compounds might be good magnetic regenerator materials for cooling below 4 K, but lower temperature heat capacity measurements need to be made to verify the actual peak heat capacity values and their magnetic ordering temperatures. However, the high cost of Rh and Ir will prohibit their widespread use as regenerator materials, regardless of their ordering temperature and heat capacity peak value.

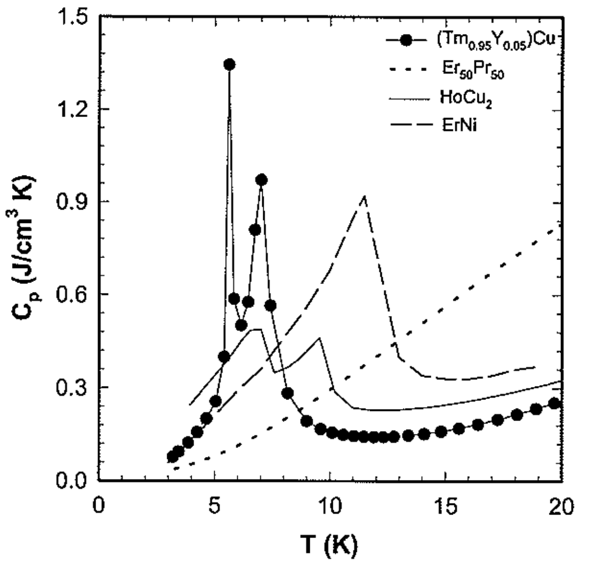

Figure 3. The volumetric heat capacity of $(Tm_{0.95}Y_{0.05})Cu$ from ~3 to 20 K. The corresponding volumetric heat capacities of the cryocooler prototype regenerator materials $Er_{50}Pr_{50}$, $HoCu_2$ and ErNi are also shown.

TmAg, which orders at 7.5 K, has a maximum heat capacity of 0.7 J/cm^{3}K, which is about 50% larger than the double peaks of $HoCu_2$, and would make an excellent replacement regenerator material for either $HoCu_2$ or Er_3Ni.

Rare Earth Additions

The substitutions of R = Sc, La, Ce, Pr and Nd for Er in $(Er_{0.9}R_{0.1})Cu$ have similar effects: the lower ordering temperature at ~8.5 K is wiped-out, the heat capacity at the upper peak (~12.7 K) is greatly reduced and shifted slightly to lower temperatures. The effect of Y is not nearly as drastic: both peaks are shifted to a lower temperature (8.5 to 7 K, and 12.7 to 12.2 K) and the magnitudes of the heat capacity peaks are greatly reduced, especially that of the 8.5 K peak. A similar behavior is observed for R substitution of Tm in TmCu, for R = La, Ce, Pr, and Nd. The substitution of Y for Tm in TmCu is, however, different from the $(Er_{1-x}Y_x)Cu$ alloys, where $0 \le x \le 0.15$. The temperatures and the peak volumetric heat capacity values of TmCu are lowered by Y doping. The upper peak temperature drops more rapidly than the lower one, so that they merge for x = 0.15. The volumetric heat capacity of $(Tm_{0.95}Y_{0.05})Cu$ is compared to those of the three low-temperature cryocooler prototype regenerator materials in Fig. 3. This alloy would be an excellent regenerator material for cooling down to 5 K.

The heavy lanthanides behave differently from the light lanthanides in that both peaks of pure ErCu still remain upon alloying. In the case of Gd and Tb dopants the peaks are shifted to a higher temperature and the volumetric heat capacities are considerably reduced. The substitution of Dy and Ho, in contrast to the other lanthanides, hardly has any affect on either the ordering temperature or the volumetric heat capacity, and Ho more so than Dy. For Dy, the temperature spread between the lower and upper ordering peaks is widened by about 2 K with low transition temperature shifted downward and the upper temperatures upward.

The substitution of Er for Tm (Tm-rich alloys) and Tm for Er (Er-rich alloys) on the volumetric heat capacity in the $(Tm_{1-x}Er_x)Cu$ pseudo binary system results in an increase of the upper heat capacity peak value of ErCu (1.4 J/cm^{3}K) to that of TmCu (2.8 J/cm^{3}K). The increase, however, is not linear, but has a sinusoid-like shape. The maximum value of the heat capacity for the lower magnetic ordering peak remains essentially constant (1.0 ± 0.3 J/cm^{3}K) as

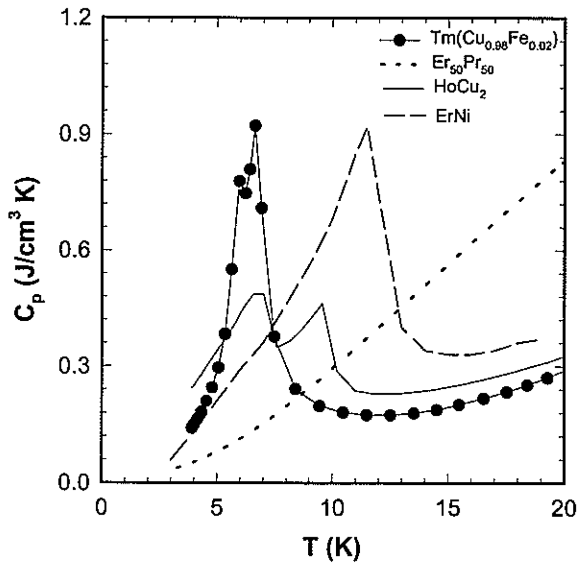

Figure 4. The volumetric heat capacity of $Tm(Cu_{0.98}Fe_{0.02})$ from ~4 to 20 K. The corresponding volumetric heat capacities of the cryocooler prototype regenerator materials $Er_{50}Pr_{50}$, $HoCu_2$ and ErNi are also shown.

x varies from 0 to 1.0. In general, as x increases, the two ordering peaks shift slowly to higher temperatures.

Transition Metal Additions

The substitution of Mn, Fe, Co, Ni and Ru for Cu in $Er(Cu_{1-x}M_x)$ and $Tm(Cu_{1-x}M_x)$ have been studied. Nominally x was 0.05, but in some cases it was as large as 0.20 and as small as 0.02. In general, the two magnetic ordering peaks of the ErCu parent compound are shifted to lower temperatures, the upper one faster than the lower ordering peak, but only in the case of Ru additions did the two ordering temperatures merge. The volumetric heat capacities are significantly lowered, with Co additions having the largest effect followed by Ni, Fe and Mn in that order.

For TmCu, the transition metal substitutes caused the two magnetic ordering peaks to merge at $x \cong 0.05$. The heat capacity values at the ordering temperature are significantly reduced, again with Co having the greatest effect followed by Ni, Ru and Fe. The volumetric heat capacity of the $Tm(Cu_{0.98}Fe_{0.02})$ ductile intermetallic compound is shown in Fig. 4 along with the prototype regenerator materials $HoCu_2$, ErNi and $Er_{0.50}Pr_{0.50}$. It is seen that the Fe doped alloy has a much better volumetric heat capacity between 5 to 8 K than $HoCu_2$. But when compared to $(Tm_{0.95}Y_{0.05})Cu$ (Fig. 3) its heat capacity values are significantly smaller.

Main Group Metal Additions

The main group metals (M = Al, Zn and Ga), when substituted for Cu in the ErCu, behave significantly different from the previous alloying agents. The lower ordering peak is shifted to higher temperatures and tends to merge with the upper magnetic ordering peak, and the heat capacity maximum is increased over the undoped ErCu material. For the Al and Ga additions at x = 0.05, these compounds have large heat capacities between 12 and 17 K (for Al), and 12 and 18 K (for Ga). The volumetric heat capacity for $Er(Cu_{0.95}Ga_{0.05})$ along with the prototype materials is shown in Fig. 5. As far as we are aware this alloy has the highest heat capacity in 15 ± 3 K range of any know material.

The effect of Al and Ga substitutions for Cu in TmCu is different from that noted above for ErCu. In the Tm-based materials, the two ordering peaks merge between the two peaks of the TmCu compound, with a volumetric heat capacity value between those of the two peaks of

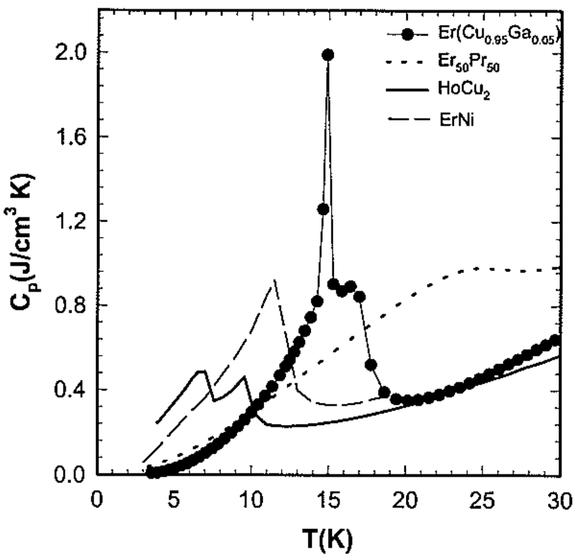

Figure 5. The volumetric heat capacity of $Er(Cu_{0.95}Ga_{0.05})$ from ~3 to 20 K. The corresponding volumetric heat capacities of the cryocooler prototype regenerator materials $Er_{50}Pr_{50}$, $HoCu_2$ and ErNi are also shown.

TmCu. For the $Tm(Cu_{0.95}Al_{0.05})$ compound, the heat capacity is three times larger than that of $HoCu_2$.

Recommended Regenerator Materials

Of the alloys studied, the best material for a regenerator which operates below 4 K is ErRh, followed closely by ErIr, see Fig. 2. But because of the cost of Rh and Ir, these two intermetallic compounds would see limited use.

There are eleven Er- and Tm-based B2 CsCl-type intermetallic compounds that could be used as a replacement for $HoCu_2$. The best is TmCu, which has a maximum heat capacity value more than six times larger than that of $HoCu_2$. However, when 5% Lu is substituted for Tm, i.e.

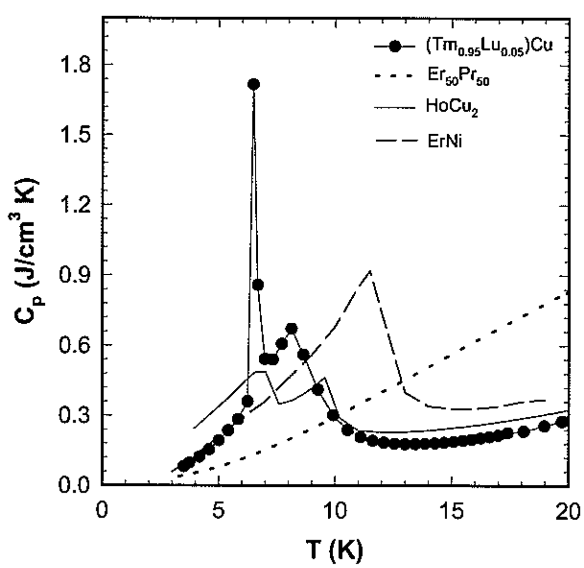

Figure 6. The volumetric heat capacity of $(Tm_{0.95}Lu_{0.05})Cu$ from ~3 to 20 K. The corresponding volumetric heat capacities of the cryocooler prototype regenerator materials $Er_{50}Pr_{50}$, $HoCu_2$ and ErNi are also shown.

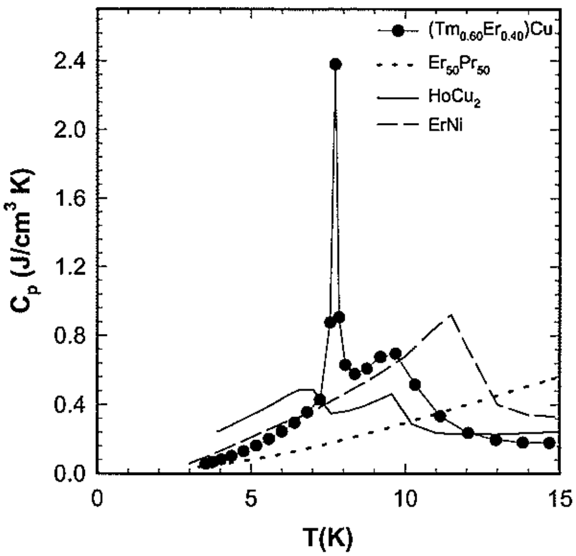

Figure 7. The volumetric heat capacity of $(Tm_{0.60}Er_{0.40})Cu$ from ~3 to 20 K. The corresponding volumetric heat capacities of the cryocooler prototype regenerator materials $Er_{50}Pr_{50}$, $HoCu_2$ and ErNi are also shown.

$(Tm_{0.95}Lu_{0.05})Cu$ the peak maximum is lowered by about half of that of TmCu, but the breadth of the pair of peaks is wider and thus is more competitive with $HoCu_2$, see Fig. 6.

In the 6 to 9 K temperature range (i.e. between the $HoCu_2$ peaks and the ErNi peak) there are four ErCu-based materials and three $(Tm_{0.6}Er_{0.4})Cu$ compounds which have significant heat capacities and could be used as regenerator materials covering this region. The best of these is $(Tm_{0.6}Er_{0.4})Cu$, see Fig. 7.

There is one $(Tm_{1-x}Er_x)Cu$ alloy which would be competitive with ErNi prototype regenerator material, namely $(Tm_{0.2}Er_{0.,8})Cu$, see Fig. 8. As a matter of fact the performance of the two materials as regenerators would be expected to be nearly the same if the two compounds

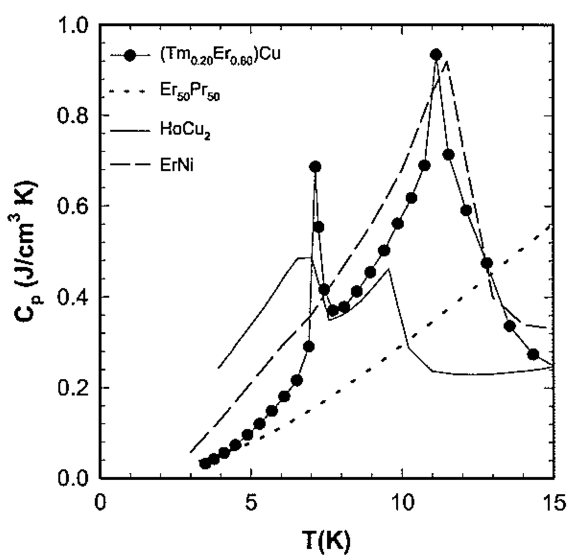

Figure 8. The volumetric heat capacity of $(Tm_{0.20}Er_{0.80})Cu$ from 3 to 20 K. The corresponding volumetric heat capacities of the cryocooler prototype regenerator materials $Er_{50}Pr_{50}$, $HoCu_2$ and ErNi are also shown.

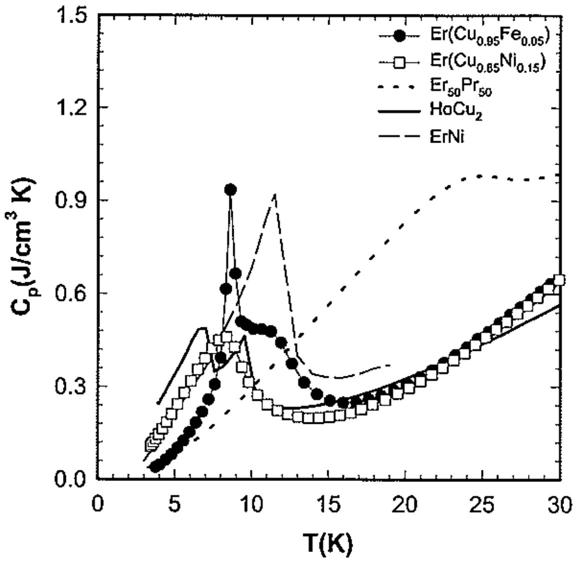

Figure 9. The volumetric heat capacities of $Er(Cu_{0.95}Fe_{0.05})$ and $Er(Cu_{0.85}Ni_{0.15})$ from ~3 to 30 K. The corresponding volumetric heat capacities of the cryocooler prototype regenerator materials $Er_{50}Pr_{50}$, $HoCu_2$ and ErNi are also shown.

were used as spheres. However, since $(Tm_{0.2}Er_{0.8})Cu$ is ductile, it can be fabricated into forms (parallel plates, monolithic perforated cylinders, etc.) which have much higher efficiencies than packed particle beds[15]. But since ErNi is a brittle intermetallic compound it is impossible, or nearly so, to fabricate into parallel plates, etc.

There is one major drawback to these Tm-based B2 intermetallic compounds, and that is the cost of Tm which can be 2 to 5 times more expensive than Er. There are, however, Er-based CsCl-type intermetallic compounds which are also better than the current prototypes, but they do not have nearly as large heat capacities as the Tm-based materials noted above. As a replacement for $HoCu_2$, the $Er(Cu_{0.85}Ni_{0.15})$ alloy is the best Er-based material, while for the 6 to 9 K temperature range $Er(Cu_{0.95}Fe_{0.05})$ would be the choice material, see Fig. 9.

For temperatures above 12 K there are three $Er(Cu_{0.95}M_{0.05})$ alloys, where M = Al, Zn and Ga, which would make excellent regenerator materials. The best being M = Ga, see Fig. 5.

SUMMARY

A large number of $(Er_{1-x}R_x)M$ and $(Tm_{1-x}R_x)M$ compounds have the B2 CsCl-type crystal structure and are also ductile. Several of them have heat capacities below 15 K, which are greater than those of the currently used prototype materials, such as $HoCu_2$, Er_3Ni and ErNi. In addition because the Er- and Tm-based intermetallics with the B2 structure are ductile, they can be easily fabricated into more efficient regenerator forms, while this is nearly impossible to do for the prototype compounds because they are brittle intermetallics. Furthermore, it has been shown that in general the Tm-based compounds are far better materials than Er-based compounds as regenerator materials because of their much higher volumetric heat capacities. When the ductile Er- and Tm-based B2 intermetallic compounds are utilized as regenerator materials for cooling below 15 K, the performances of cryocoolers will be improved, their efficiencies increased, and the no load temperatures will be lower as compared to the currently utilized regenerator materials ($HoCu_2$, Er_3Ni and ErNi).

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