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Development of Dispersion-Strengthened XD™ Cu Alloys for High Heat-Flux Applications

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DEVELOPMENT OF DISPERSION-STRENGTHENED XD™ Cu ALLOYS

FOR HIGH HEAT-FLUX APPLICATIONS

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Abstract

In a previous effort sponsored by the NASA Lewis Research Center, the XD™ process was used to produce ZrB_2 particulate reinforcements in Cu and the resulting extruded material was microstructurally characterized and evaluated in tension over a range of temperatures. A problem that was encountered in that study was microstructural inhomogeneity resulting from the frequent presence of "ZrB_2 agglomerates" that were several microns in size. The presence of these agglomerates was attributed to improper mixing of powders in the green compact used in the XD™ process and specifically, to elemental boron powder segregation.

In this program, several milling parameters were examined in an effort to optimize this processing step; two levels of ZrB_2 reinforcements were considered (7 vol.% and 15 vol. %). Microstructures of the reacted powder mass were examined to verify the absence of these agglomerates. Larger batches of powder were then mixed, reacted, machined to size, canned and extruded. The microstructure and tensile properties of these extrusions were examined, and the measured properties were correlated with the observed microstructure. Large unreacted or partially reacted Zr particles were present that affected the mechanical properties deleteriously and their presence is attributed to insufficient heat of reaction during XD™ synthesis. Alternate processing routes are recommended.

CONTENT

EXECUTIVE SUMMARY

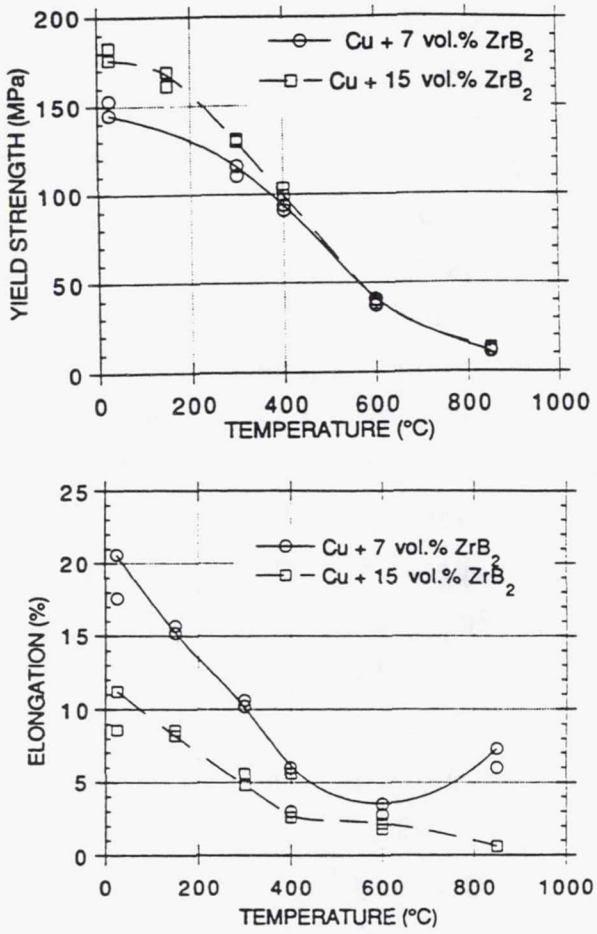
Improved copper-based alloys are being examined as potential candidate materials for rocket thrust chamber liners to improve performance and durability. In a previous effort sponsored by the NASA Lewis Research Center, the XD™ process was used to produce ZrB_2 particulate reinforcements in Cu and the resulting extruded material was microstructurally characterized and evaluated in tension over a range of temperatures. In general, these reinforced alloys were claimed to exhibit good strength and thermal conductivity, and more importantly, they were claimed to retain respectable strengths at the intended use temperatures. One problem that was encountered in that study was microstructural inhomogeneity resulting from the frequent presence of "ZrB_2 agglomerates" that were several microns in size.

In the present program, several milling parameters were examined in an effort to optimize this processing step as it was believed that the ZrB_2 agglomerates were a consequence of improper mixing; two levels of ZrB_2 reinforcements were considered (7 vol.% and 15 vol. %). After identifying the processing parameters to obtain uniform mixing, sufficient quantities of material were produced, canned, extruded and characterized in terms of their microstructures and mechanical properties.

Standard cylindrical tensile specimens were machined from the extruded material containing 7 and 15 vol.% ZrB_2 and tested in the temperature range 25°C - 850°C. The variations in yield strength and ductility with test temperature are shown in the figure below. For both reinforcement levels, the strength and ductility decrease rapidly with increasing temperature. Polished guage sections of fractured tensile specimens of the 7 vol.% ZrB_2 reinforced material revealed localized necking in the 25°C specimen whereas this was not evident in the 400°C specimen. Instead several surface cracks were seen in the latter. In both cases, large particles were seen (as large as 50 μm), fairly uniformly distributed throughout the section. Higher magnification micrographs of these individual particles revealed a reaction zone that extended to a significant depth within the particles. From these observations, it appears unlikely that these large particles are agglomerates of ZrB_2 and more likely unreacted or partially reacted Zr particles, where the reacted zone could be either a ternary Zr-Cu boride or simply a binary Zr-Cu intermetallic. Differential thermal analysis showed several minor endotherms during the heating cycle (in the

temperature range 800°C to 925°C) before complete melting occurs at ~1000°C. During cooling, solidification commences at about the melting point of Cu and is complete fairly soon thereafter; below 1050°C, no further exotherms or endotherms were observed suggesting that the minor endotherms observed during heating are likely a consequence of low-melting metastable phases. These metastable phases can result from incomplete reactions during the XD™ synthesis.

Fracture surfaces of specimens tested at temperatures above 400°C were severely oxidized and could not be characterized. Whether this is a consequence of the presence of unreacted Zr or is inherent to the material due to the presence of ZrB_2 could not be ascertained in this study but requires further attention. Finally, alternate processing routes are recommended to circumvent the problems encountered in this study.



Variation in yield strength and ductility with test temperature for Cu - 7 vol.% ZrB_2 and Cu - 15 vol.% ZrB_2 alloys produced using XD™ synthesis.

I. INTRODUCTION

Improved copper-based alloys are being examined as potential candidate materials for rocket thrust chamber liners to improve performance and durability. Copper and its alloys typically exhibit desirable thermal conductivity and if their ability to retain strength at elevated temperatures can be improved, they would be very attractive for such applications. In a previous effort sponsored by the NASA Lewis Research Center, the XD™ process was used to produce ZrB_2 particulate reinforcements in Cu and the resulting extruded material was microstructurally characterized and evaluated in tension over a range of temperatures. In general, these reinforced alloys were claimed to exhibit good strength and thermal conductivity, and more importantly, they were claimed to retain respectable strengths at the intended use temperatures. One problem that was encountered in that study was microstructural inhomogeneity resulting from the frequent presence of "ZrB_2 agglomerates" that were several microns in size. Such "clumps" can act as flaws and initiate premature failure in the alloy. The source of these agglomerates was identified as being improper mixing of powders in the green compact used in the XD™ process and specifically attributed to elemental boron powder segregation. It was then argued that if the mixing step was optimized to obtain a uniform distribution of the elemental powders, then such "ZrB_2 agglomerates" could be eliminated or at least, drastically reduced in content. Based on these findings, a follow-on program was initiated to address this problem.

In this program, several milling parameters were examined in an effort to optimize this processing step; two levels of ZrB_2 reinforcements were considered (7 vol.% and 15 vol. %). After identifying the processing parameters to obtain uniform mixing, sufficient quantities of material were produced, canned, extruded and

characterized in terms of their microstructures and mechanical properties.

II. TECHNICAL BACKGROUND

In the previous program, copper containing 7 and 15 vol.% ZrB_2 particulate were produced by the XD™ process and characterized in the as-extruded, extruded and HIPed, and extruded and heat-treated conditions. The results of room temperature tensile studies on such materials are summarized in Table I. Neither HIPing nor heat treatment appear to have any effect on the as-extruded, room temperature tensile properties. The effect of test temperature on the yield strength, UTS and elongation are summarized in Table II. Strength decreases with increasing temperature at a similar rate for both levels of reinforcements although, in terms of absolute values, the 15 vol.% material remains stronger at all temperatures tested. The ductility of the 15 vol.% reinforced material is very low at all temperatures tested, although curiously enough, it reaches a maximum at an intermediate temperature before decreasing again at higher temperatures. The 7 vol.% reinforced material also reveals a similar behavior, although much higher ductilities are obtained. The poor ductility in the 15 vol.% reinforced material is likely a direct consequence of the agglomeration problem, considering that these ductilities are in a nominally pure copper matrix. The initial increase in ductility with test temperature can then be expected; what is difficult to explain is the ductility loss beyond the maximum (i.e. ~6.4% at 800 F in the 15 vol.% material and ~16.4% at 400 F in the 7 vol.% material; Table II) with increasing temperatures at temperatures that are ~0.7 T_m. Three possible scenarios that come to mind are: a) interfacial cavitation at the Cu/ZrB_2 interface, b) incipient melting due to the presence of either a low melting ternary phase or a metastable binary phase, and c) environmental embrittlement (air).

The first of these two possibilities can be recognized by examining tensile specimen cross sections adjacent to the fracture surface, particularly those that have been tested at high temperatures. The second factor is a little more difficult to confirm

Table I: Effect of processing on the room temperature tensile properties of Cu - ZrB_2 composites; strain rate = $1.3 \times 10^{-3}\ s^{-1}$.

Material	Condition	YS (MPa)	UTS (MPa)	Elong. (%)
Cu - 15 vol.% ZrB2	As - Ext.	376	498	2.1
(188)	As - Ext.	375	506	4.9
Ext. + HIP (900°C/4h/104 MPa)		389	504	1.9
Ext. + HIP (900°C/4h/104 MPa)		388	497	2.0
Ext. + 900°C/4h		367	489	2.3
Ext. + 900°C/4h		359	490	2.2
Cu - 7.5 vol.% ZrB2	As - Ext.	215	318	10.9
(189)	As - Ext.	221	335	10.6
Ext. + HIP (900°C/4h/104 MPa)		208	315	12.4
Ext. + HIP (900°C/4h/104 MPa)		195	311	13.3
Ext. + 900°C/4h		201	309	11.7
Ext. + 900°C/4h		202	307	11.6

Table II: Effect of temperature on the tensile properties of Cu - ZrB_2 composites in the extruded and HIPed condition; strain rate = $6.6 \times 10^{-4}\ s^{-1}$.

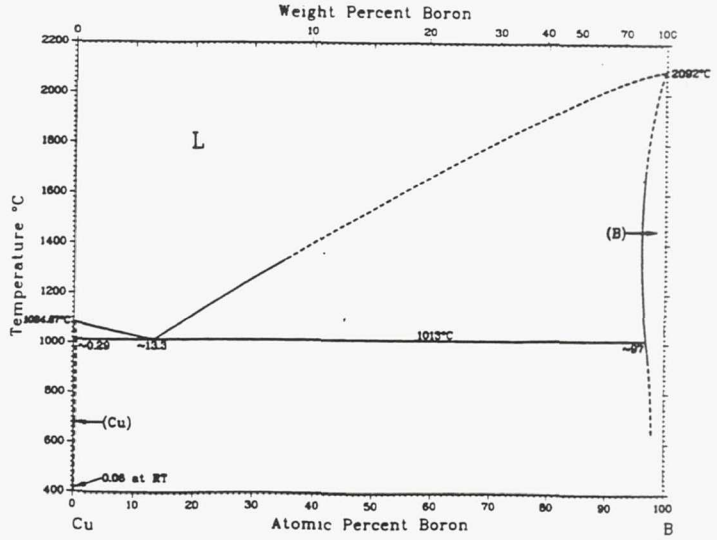
Material	Test Temp. (°C)	YS (MPa)	UTS (MPa)	Elong. (%)
Cu + 15 vol.% ZrB_2	25	389	504	1.9
(188 Ext + HIP)	25	388	497	2.0
	205	351	385	3.5
	205	353	398	2.7
	425	196	206	6.4
	425	185	195	4.8
	538	133	185	6.0
	538	155	158	2.0
	648	105	109	3.1
	760	68	68	2.4
	760	77	80	2.0
Cu + 7.5 vol.% ZrB_2	25	208	315	12.4
(189 Ext + HIP)	25	195	311	13.3
	205	187	241	14.6
	205	186	243	16.4
	425	132	145	12.3
	425	131	143	13.1
	538	97	103	6.7
	648	59	61	9.5
	648	69	71	5.8
	648	70	70	6.2
	760	43	44	6.0

especially if a ternary phase diagram is not available, as is the case (to the best of our knowledge) for the Cu - Zr - B system. In fact, even a single ternary isotherm could not be found for this system. Superimposed on this problem is the possible presence of low melting metastable phases that can occur due to the specific processing route adopted in this and the previous program.

Even though the ternary isotherms for this system are currently unavailable, a lot of insight into the ternary alloys can be obtained by carefully examining the binary phase diagrams. The binary Cu-B, Cu-Zr and the Zr-B phase diagrams are shown in Figure 1a-c. The Cu-B system is a simple eutectic system with a eutectic composition of ~13.3% B and an associated temperature of 1013°C. Likewise in the Cu-Zr system, a eutectic reaction occurs at ~6 % Zr and a temperature of 966°C ; further, in this system, several intermetallics are formed in the 30 - 70 at.% Zr range that result in fairly low temperature eutectics (e.g. 886°C between δ and ε in Figure 1b) so that if such metastable Cu-Zr phases remain after the XD™ synthesis step, they may cause preferential weakening at the Cu/metastable-phase interface. In addition, if substantial amounts of elemental Zr or Zr-rich phases are present, they may readily oxidize at elevated temperatures during testing and can provide preferential crack paths.

Since in this program, and in the previous one, the region of interest to us is the Cu-ZrB_2 system, it is also necessary to examine the Zr-B binary diagram (Figure 1c). In this system there are two borides, ZrB_2 and ZrB_{12}; the lowest temperature where liquid is present is ~1680°C and is therefore not a concern as Cu melts at a much lower temperature of 1083°C. It is therefore not unreasonable to anticipate a pseudobinary section to exist along the Cu-ZrB_2 system and this is schematically illustrated in Figure 2a where some of the information from Figure 1a-c are simply laid out on the sides of a triangle that schematically constitutes the ternary space. If we now assume that a pseudobinary exists between Cu and ZrB_2, the next feature that is

a



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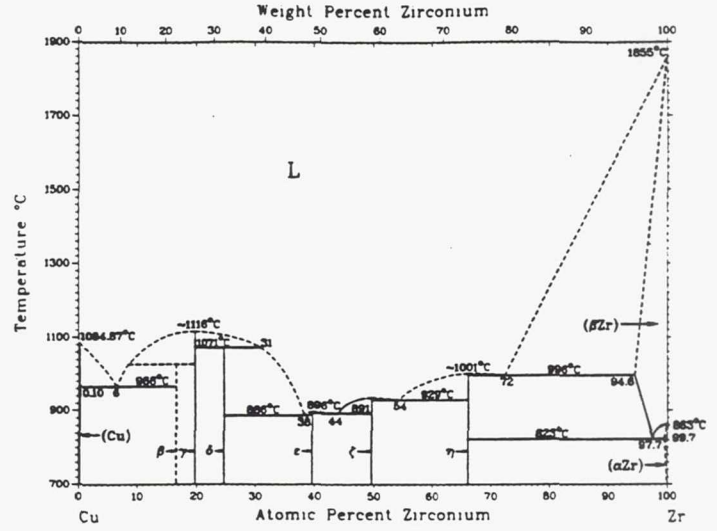

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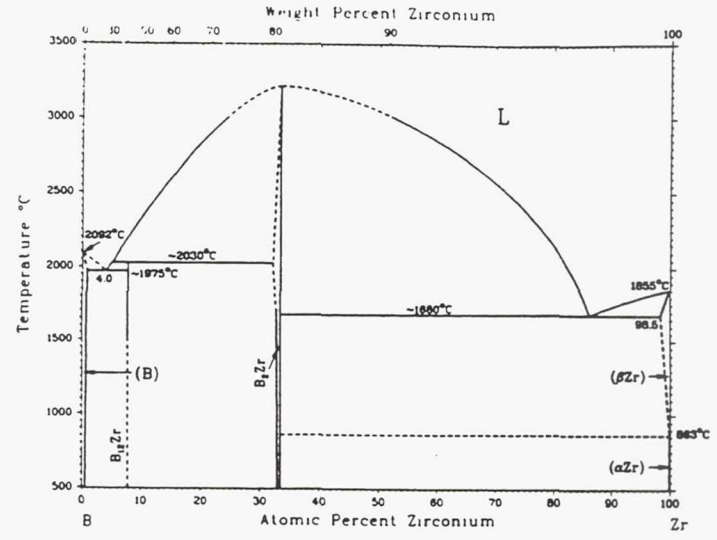


Figure 1. The binary phase diagrams for (a) Cu-B, (b) Cu-Zr, (c) Zr-B systems.

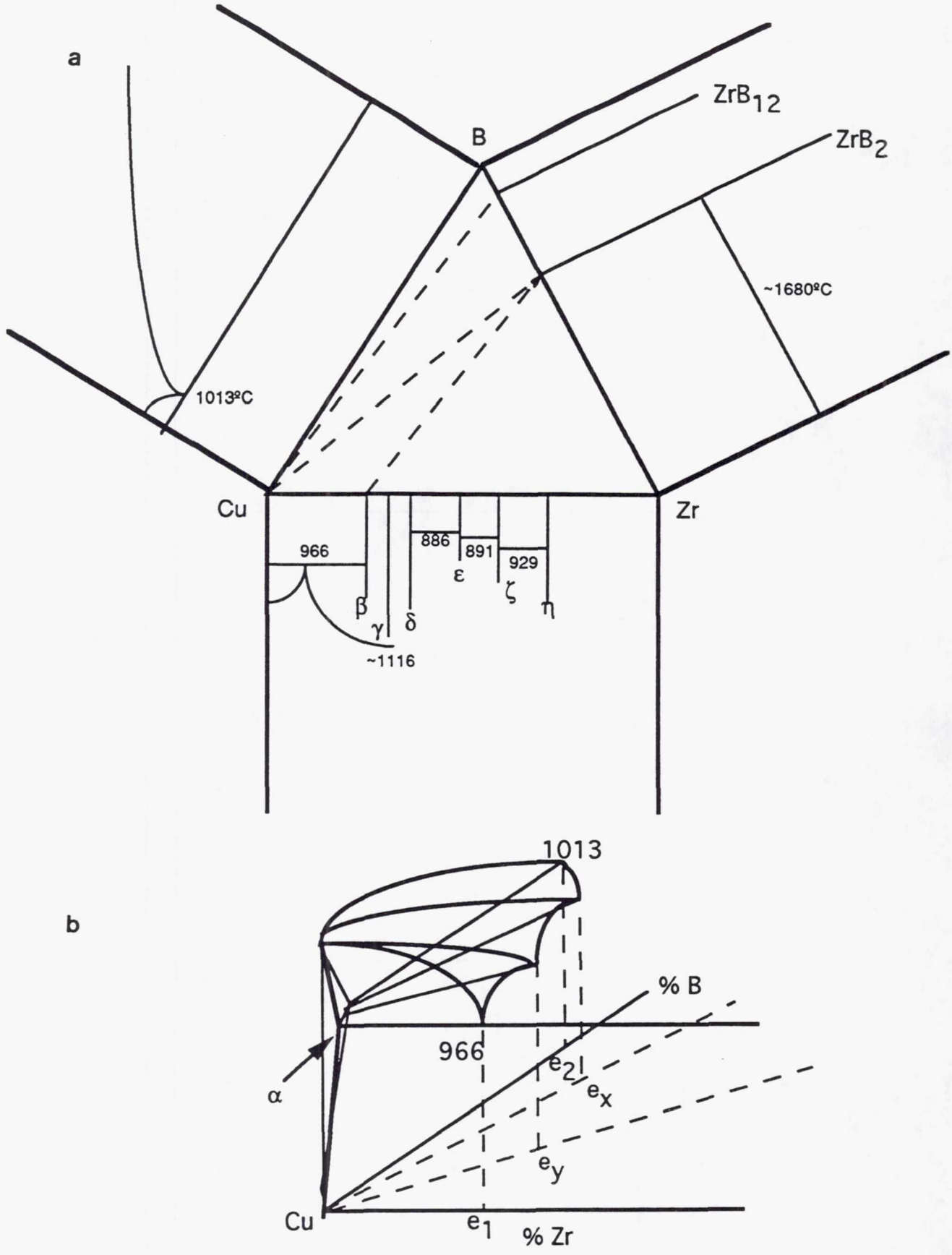


Figure 2. A schematic arrangement of the three binary diagrams on the sides of a triangle constituting ternary space (a) and, a possible ternary phase diagram in the Cu-rich corner (b).

relevant is the type of phase diagram as this will influence the lowest temperature at which liquid can exist in this system. If a stable two-phase region does not exist between Cu and ZrB_2 (i.e. absence of a pseudobinary), then it implies that ZrB_2 is not thermodynamically stable in Cu. If the pseudobinary is of the peritectic type, then the lowest temperature at which liquid will be present is likely to be the melting point of pure Cu (1083°C); this appears unlikely as at the Cu-rich end in the Cu-Zr and Cu-B systems, eutectic reactions occur. It is therefore thought that the Cu-ZrB_2 pseudobinary also exhibits a eutectic reaction which means that the lowest temperature at which a liquid can exist will be below the melting point of Cu. A schematic of the ternary section at the Cu-rich end, based on the above arguments is provided in Figure 2b. In this Figure, the L + α region is shown, and e_x and e_y are pseudobinary eutectic compositions. The possible presence of a ternary eutectic (invariant) and ternary phases have not been considered. If the above described scenario is true, then the pseudobinary eutectic temperature will determine the temperature at which liquid first forms on heating.

III. SCOPE OF THE PRESENT EFFORT

In this program, the processing parameters prior to the XD™ synthesis step for producing ZrB_2 particulate-reinforced Cu at 7 and 15 vol.% levels was examined in an attempt to eliminate the inhomogeneous distribution of the particulate and to resolve the issue of particle agglomeration. Material produced after optimizing these processing parameters was to be canned and extruded. A part of the extrusions was to be provided to the NASA Lewis Research Center for their internal evaluation. Tensile tests were to be conducted as a function of temperature from the remaining material in the temperature range 298K (25°C) - 1123K (850°C) and the resulting properties correlated with the observed microstructures. The detailed technical part of the statement of work as it appears in the contract is reproduced in the next chapter. It is also pertinent to indicate at this point that this program transitioned through three principal investigators (R.M. Aikin Jr. in the initial stages, L. Christodoulou in the intermediate stages and K.S. Kumar during the last two months of the program), as a consequence of which, the interpretation in this report of the obtained results are those of the author (K.S. Kumar); in addition, the current author, based on his interpretation of the results did not have the resources to consider alternate experiments and instead has provided some recommendations for future direction.

IV. STATEMENT OF WORK

Objective

The objective of this effort is to experimentally find "XD" processing parameters capable of producing a dispersion strengthened Cu alloy having a uniform dispersion of submicron sized borides or carbides and to evaluate the properties of these alloys to determine their suitability for use as rocket engine combustion chamber liners.

Task I. Synthesis Studies

The contractor shall perform the following:

Small samples of Cu alloys with carbides or borides shall be synthesized using various processing and consolidation conditions to produce a uniform fine dispersion. The alloys shall have from 7 to 15 volume percent dispersoid. Metallography shall be used to assess the quality of the dispersions. Particle size and spatial distributions shall be characterized as a function of the synthesis and consolidation parameters. The role of the synthesis and consolidation variables on oxygen, carbon and other detrimental contaminants shall be studied.

On completion of the task, the contractor shall select, with the approval of the NASA Technical Program Manager, a preferred set of synthesis and consolidation parameters to fabricate bar stock in Task II for mechanical property evaluation and delivery to NASA LeRC.

Task II. Bar Stock Fabrication

After receiving approval of the preferred set of synthesis and consolidation parameters from the NASA Technical Program Manager, the contractor shall fabricate random lengths of bar stock of approximately 1.3 cm diameter. The total length of the bar stock shall be 5 to 10 meters for each of two compositions. At least a total length of 3.25 meters of the bar stock for each composition shall be delivered to the NASA Lewis Research Center. The remainder shall be studied by the contractor in Task III.

Task III. Property Evaluations

The contractor shall evaluate the short time tensile strength of the alloys from Task II from room temperature to 850°C. These alloys shall be metallurgically evaluated.

Task IV. Program Management and Reports

Monthly and Final report as per the requirements in the contract.

V. RESULTS AND DISCUSSION

1. Synthesis studies:

As previously suggested, the source of the agglomeration problem and the presence of large ZrB_2 particles was thought to lie in inadequate mixing of the elemental powders and specifically, inhomogeneous distribution of boron. So, in this effort, appropriate amounts of Cu (-325 mesh; ≤ 44μm), Zr (-100 mesh; ≤ 150 μm) and submicron boron powders to yield a Cu-15 vol.% ZrB_2 composite were blended in a ball mill for 4h, cold pressed into a compact, exothermally reacted and optically characterized. Representative micrographs in Fig. 3a,b reveal that the mixing is insufficient to eliminate the "coarse particles". These particles, originally believed to be large ZrB_2 particles, are now argued to be elemental Zr (or partially alloyed with Cu) that simply did not react to form the borides. These particles are anywhere from 5 - 50 μm in size and lie within the starting Zr powder size range. This would not be entirely surprising considering that 15 vol.% ZrB_2 would not be able to sustain a vigorous exothermic reaction in a conductive material like Cu, therefore leaving an incomplete product. Further evidence for this argument follows in section 2, relating to the microstructure of the extruded material.

It was then argued that conventional ball-milling did not impart sufficient energy to obtain the desired degree of mixing and therefore, a more vigorous approach involving attrition-milling using zirconia grinding medium was examined. Once again, a Cu-15 vol. % ZrB_2 material was evaluated. Representative micrographs of the as-reacted material that had been previously subjected to 4, 8 and 16h of milling are shown in Fig. 4a-c respectively. Even after 16h of milling, large strung-out particles are seen at the boundaries of the Cu particles, which themselves have been severely deformed, welded, fractured and rewelded several times as would be expected in

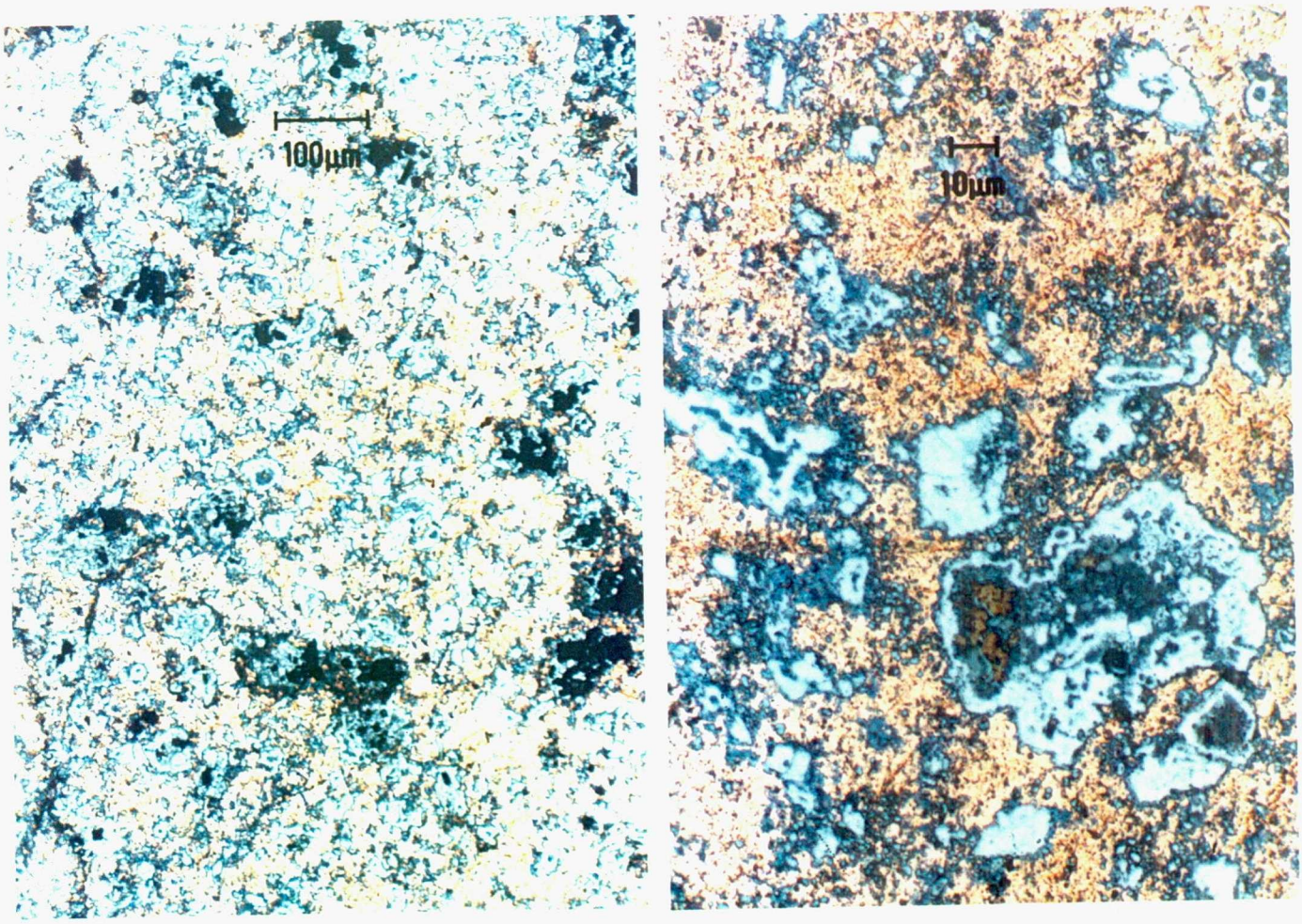


Figure 3. The microstructures (a, b) of as-reacted Cu-15 vol.% ZrB_2 after the starting powders had been ball-milled for 4h.

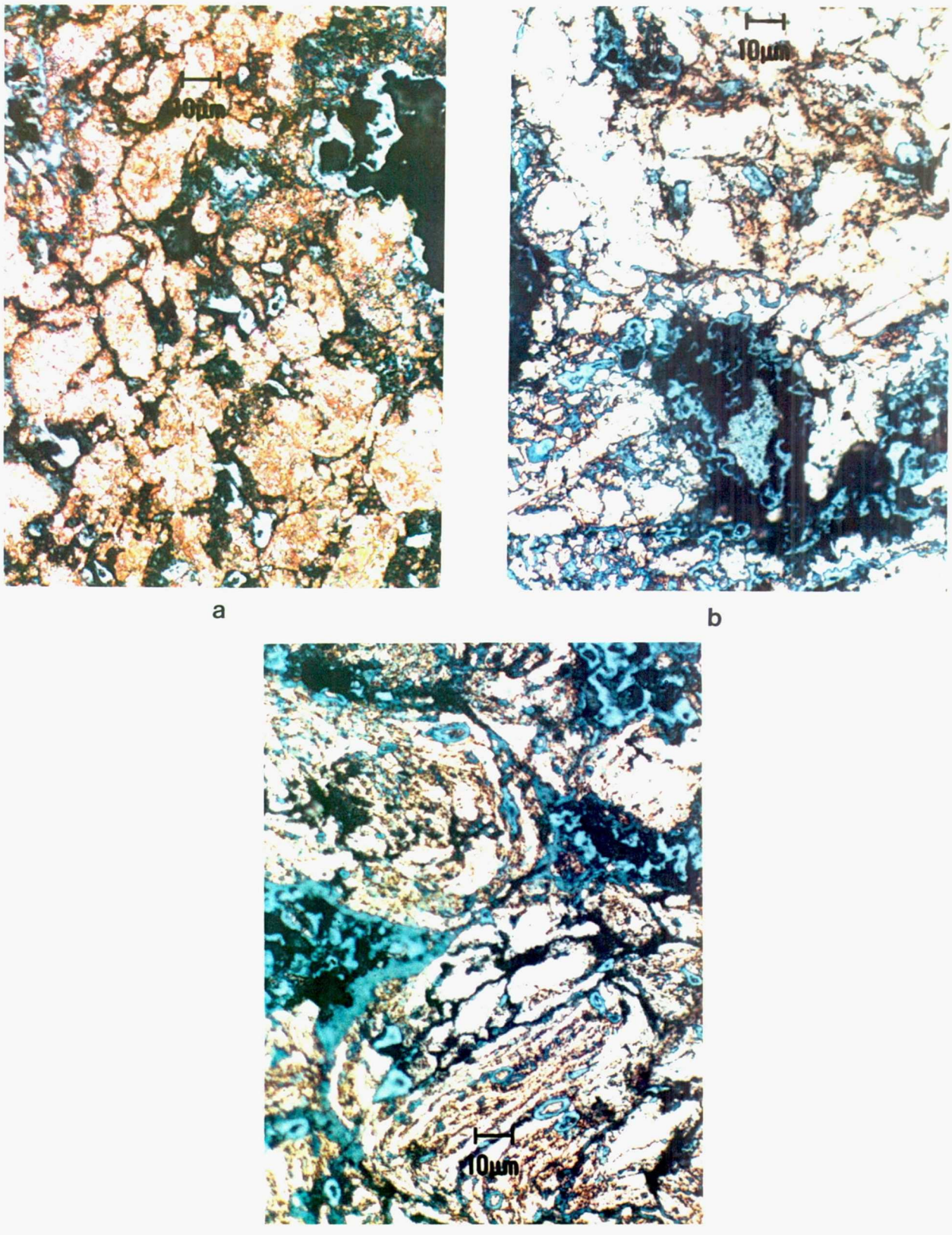


Figure4. The microstructures of as-reacted Cu-15 vol.% ZrB_2 after the starting powders were attrition-milled using zirconia medium for (a) 4h, (b) 8h, and (c) 16h.

high-energy milling. Clearly, the ligaments around these Cu particles, previously identified as ZrB_2, have no metallurgical reason to assume that shape and lend credence to the argument that they are simply unreacted Zr particles that have been kneaded into the Cu. Even 16h of attrition-milling using zirconia grinding medium was deemed insufficient and therefore a third study was initiated, this time using WC balls instead of zirconia as the grinding medium, and both, a 7.5 vol.% and a 15 vol.% ZrB_2 material were examined. Microstructural changes accompanying extended milling times for the 7.5 vol.% material are seen in Fig. 5a-c and those for the 15 vol.% material in Fig. 6a-c. Essentially, there is not a significant difference in the sequence of microstructures in these two sets of figures as compared to Fig. 4a-c, except that there is a marginal increase in the severity of milling that is reflected in the microstructures. It was felt at that stage, that ~8h of milling using an attrition mill with WC grinding balls was sufficient to produce a reacted microstructure that was acceptable.

It should also be emphasized that the efficiency of milling is dependent amongst other factors, on the ratio of powder to grinding medium and on the duration of milling. Thus, optimal milling time obtained using a certain experimental batch size cannot be directly transitioned to a bigger batch size that would be necessary to produce the bar stock for the next task.

2. Bar Stock Fabrication:

Eight billets, three containing 7 vol.% ZrB_2 and five containing 15 vol.% ZrB_2 were prepared using XD™ synthesis and "optimal" parameters identified in the previous task. These as-reacted compacts were machined to shape after a hydrogen anneal, canned, and extruded at the NASA Lewis Research Center. (The author acknowledges Dr. J.D. Whittenberger for his assistance and cooperation in extruding these materials at NASA Lewis Research Center at short notice). The initial canned billets were 3" in diameter and 5.5" long. A reduction ratio of 24:1 and an extrusion

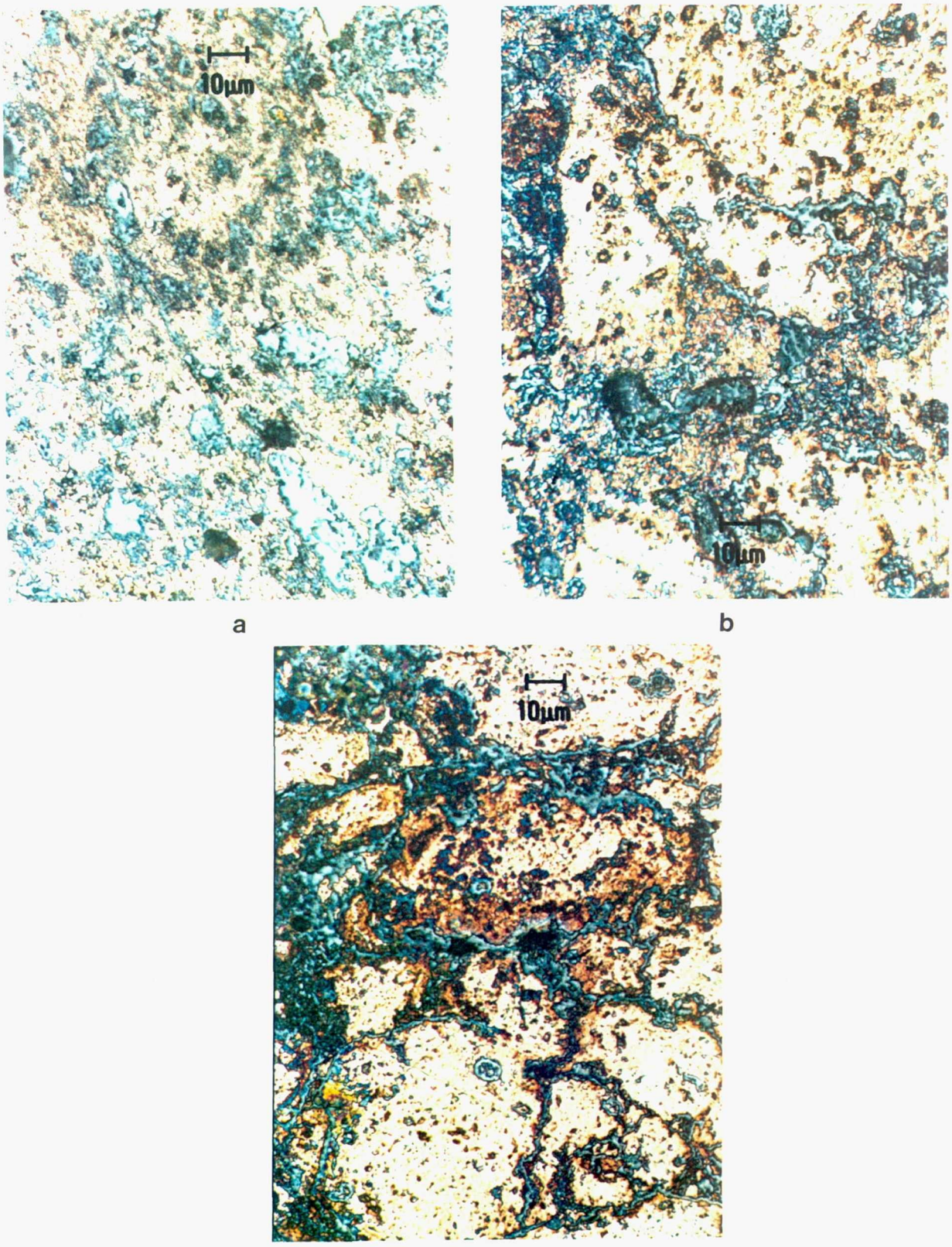


Figure 5. The microstructures of as-reacted Cu-7.5 vol.% ZrB_2 after the starting powders were attrition-milled using WC medium for (a) 4h, (b) 8h, and (c) 9.5h.

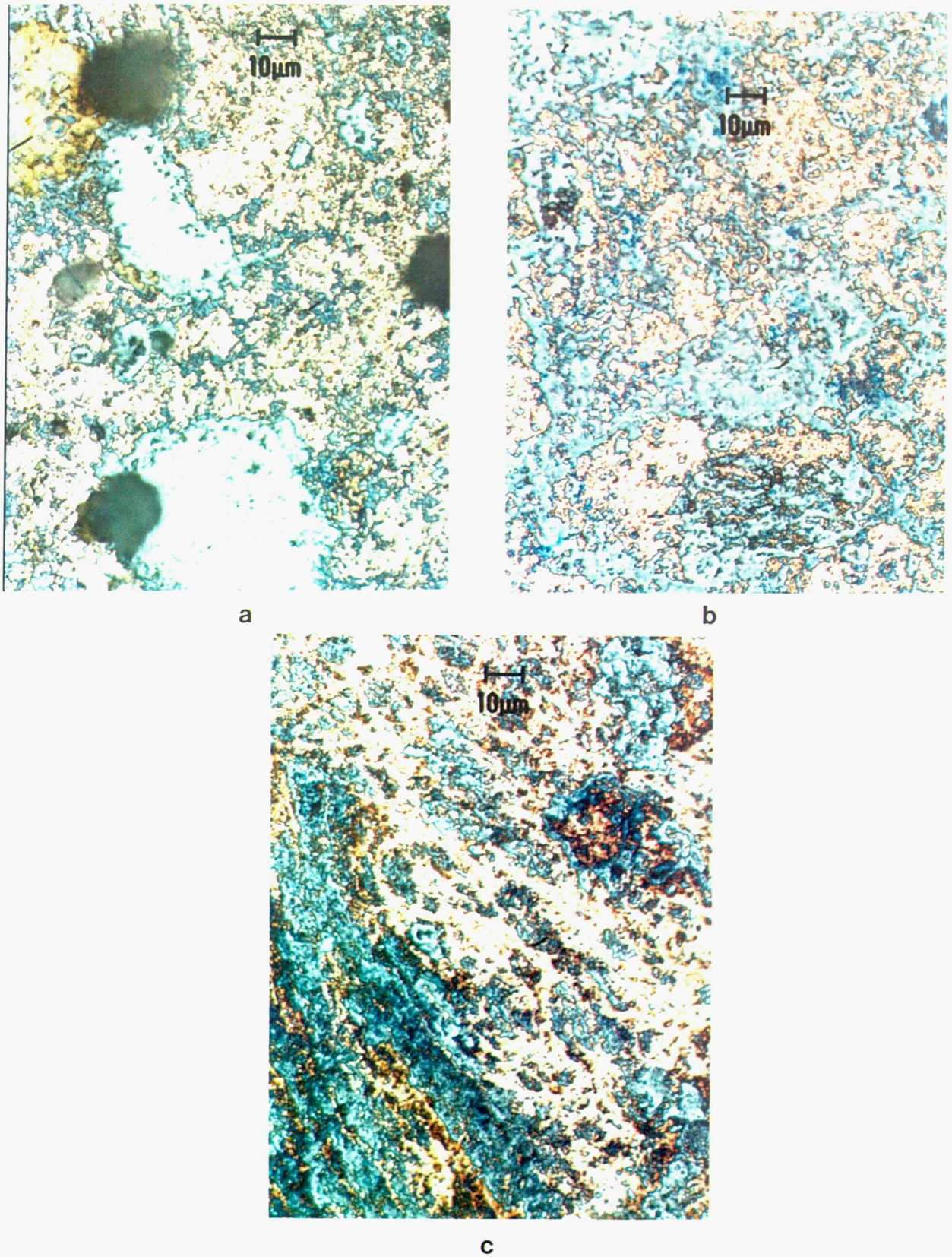


Figure 6. The microstructures of as-reacted Cu-15 vol.% ZrB_2 after the starting powders were attrition-milled using WC medium for (a) 4h, (b) 8h, and (c) 10.25h.

temperature of 850°C were used. Details of the extrusion parameters and post extrusion observations are provided in the Appendix for some of the extrusions. Most of the material extruded well, although in some cases, the specimen broke through the can. A part of the extrusions were left behind at the NASA Lewis Research Center for internal evaluation as required by the contract.

3. Material Characterization

Standard cylindrical tensile specimens were machined from the extruded material containing 7 and 15 vol.% ZrB_2 and tested in the temperature range 25°C - 850°C. Duplicate specimens were tested at each temperature. Yield strength, ultimate tensile strength and plastic elongation to failure were measured in each case and documented in Table III. The variations in strength and ductility with test temperature are shown in Fig. 7-9. For both reinforcement levels, the strength at room temperature is significantly lower than those recorded in the previous study (see Table II) for the corresponding materials. The variation in ductility with temperature of the composites in this study is similar to previous observations in that a decrease in ductility with increasing temperature is noted; however, the absolute values of elongation are significantly higher for each of the composites in the present study relative to those previously observed. Reasons for the decrease in ductility with increasing temperature are discussed in the post-deformation microstructural analysis section.

4. Post-Deformation Microstructural Analysis

Guage sections of fractured tensile specimens of the 7 vol.% ZrB_2 reinforced material were polished and optically examined. Representative micrographs of the specimen tested at room temperature and at 400°C are shown in Fig. 10a, b respectively. Localized necking is seen in the 25°C specimen whereas this is not

Table III: Tensile properties of extruded Cu - ZrB_2 composites produced in this program.

Material	Test Temp. (°C)	YS (MPa)	UTS (MPa)	Elong. (%)
Cu + 15 vol.% ZrB_2	25	389	504	11.2
	25	388	497	8.6
	150	351	385	8.2
	150	353	398	8.6
	300	196	206	4.8
	300	185	195	5.6
	400	133	185	2.6
	400	155	158	5.6
	600	105	109	1.8
	600	68	68	2.2
	850	77	80	0.6
Cu + 7 vol.% ZrB_2	25	208	315	20.6
	25	195	311	17.6
	150	187	241	15.2
	150	186	243	15.7
	300	132	145	10.2
	300	131	143	10.6
	400	97	103	6.0
	400	59	61	3.0
	600	69	71	3.5
	600	70	70	2.8
	850	43	44	7.3
	850	12	12.5	6.0

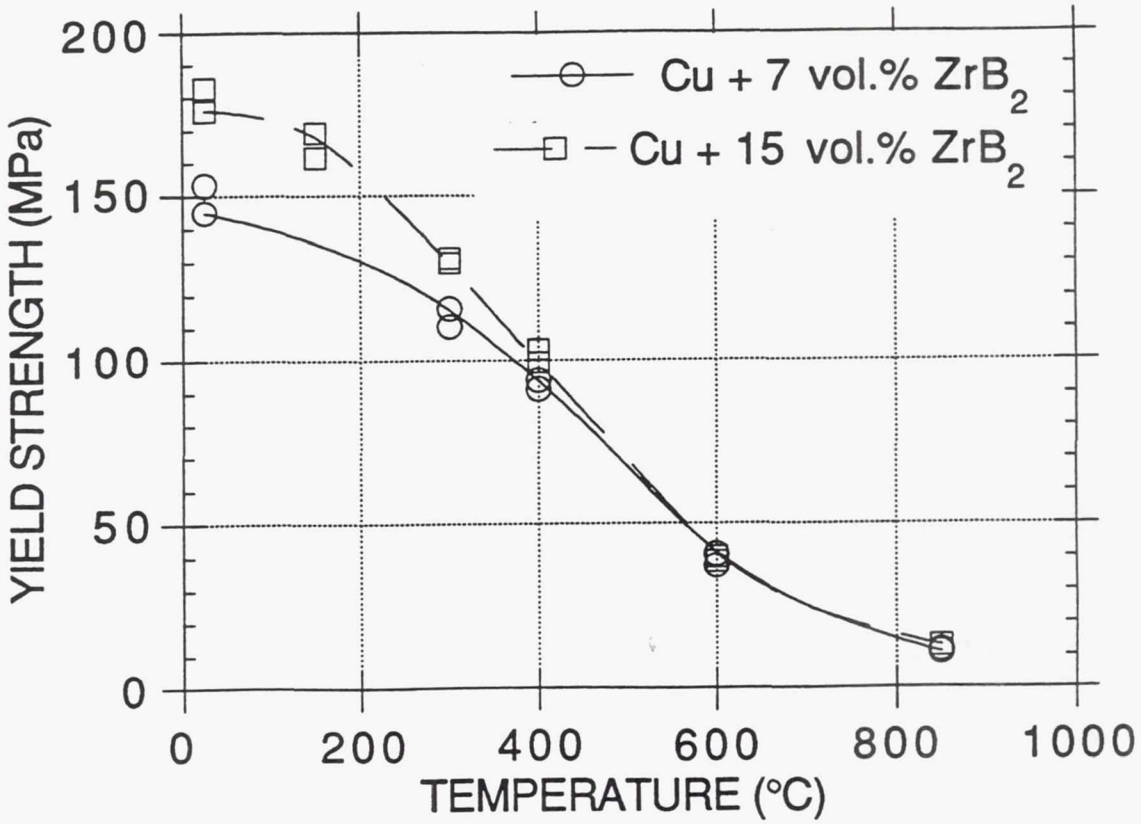


Figure 7. The tensile yield strength - temperature profile for the extruded composites containing 7 vol.% and 15 vol.% ZrB_2 reinforcement.

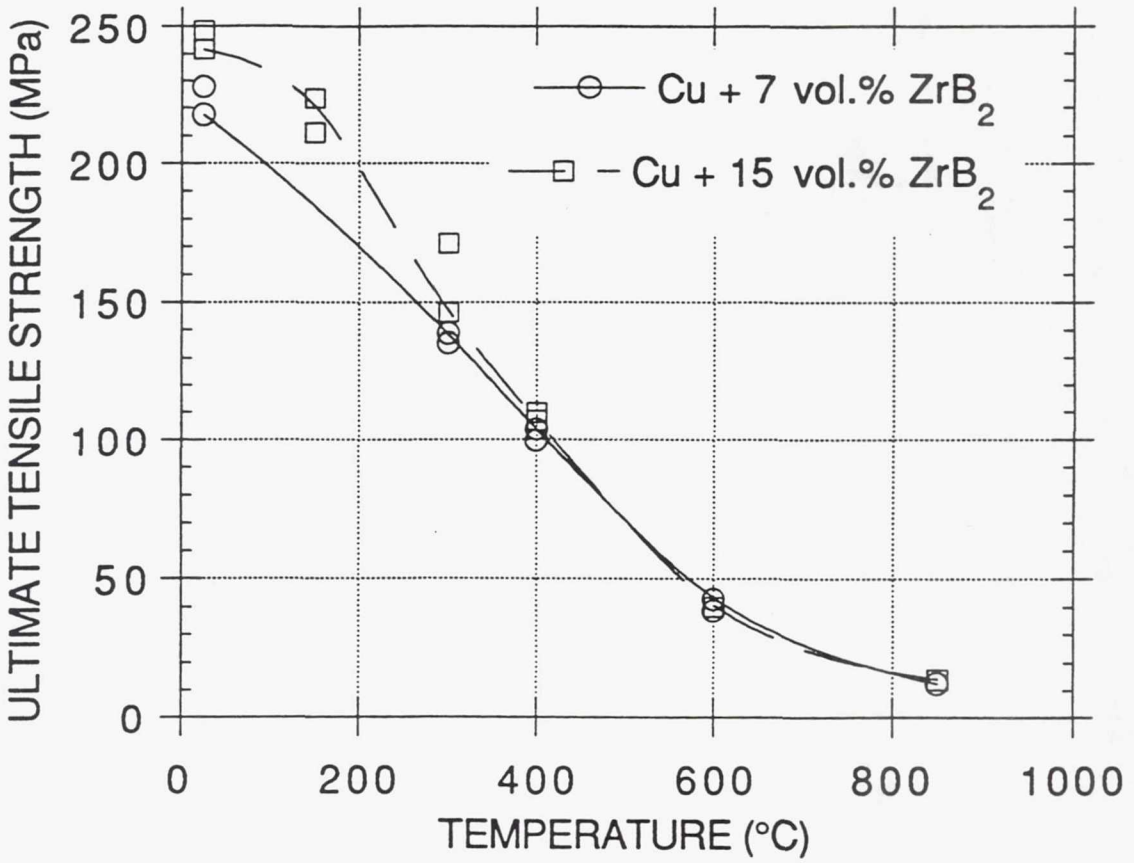


Figure 8. Variation in ultimate tensile strength with temperature for the extruded Cu - 7 vol.% ZrB_2 and Cu - 15 vol.% ZrB_2 composites.

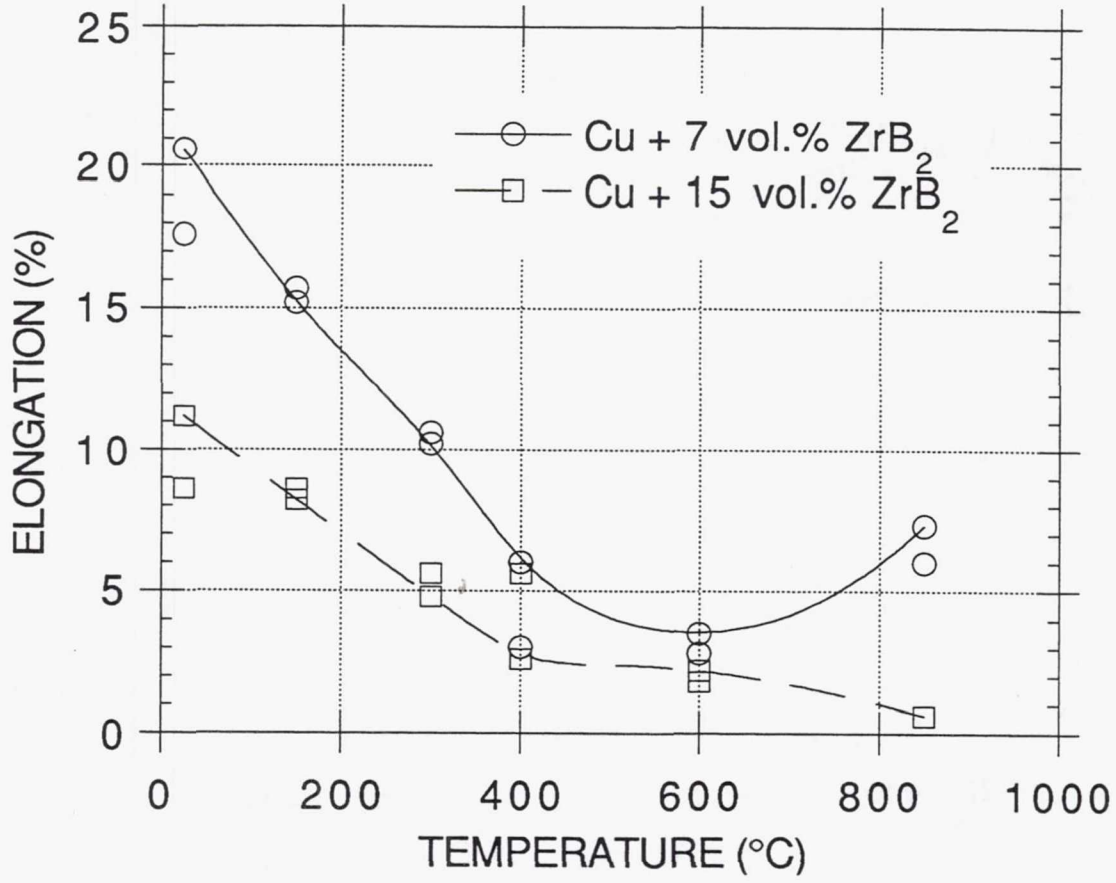
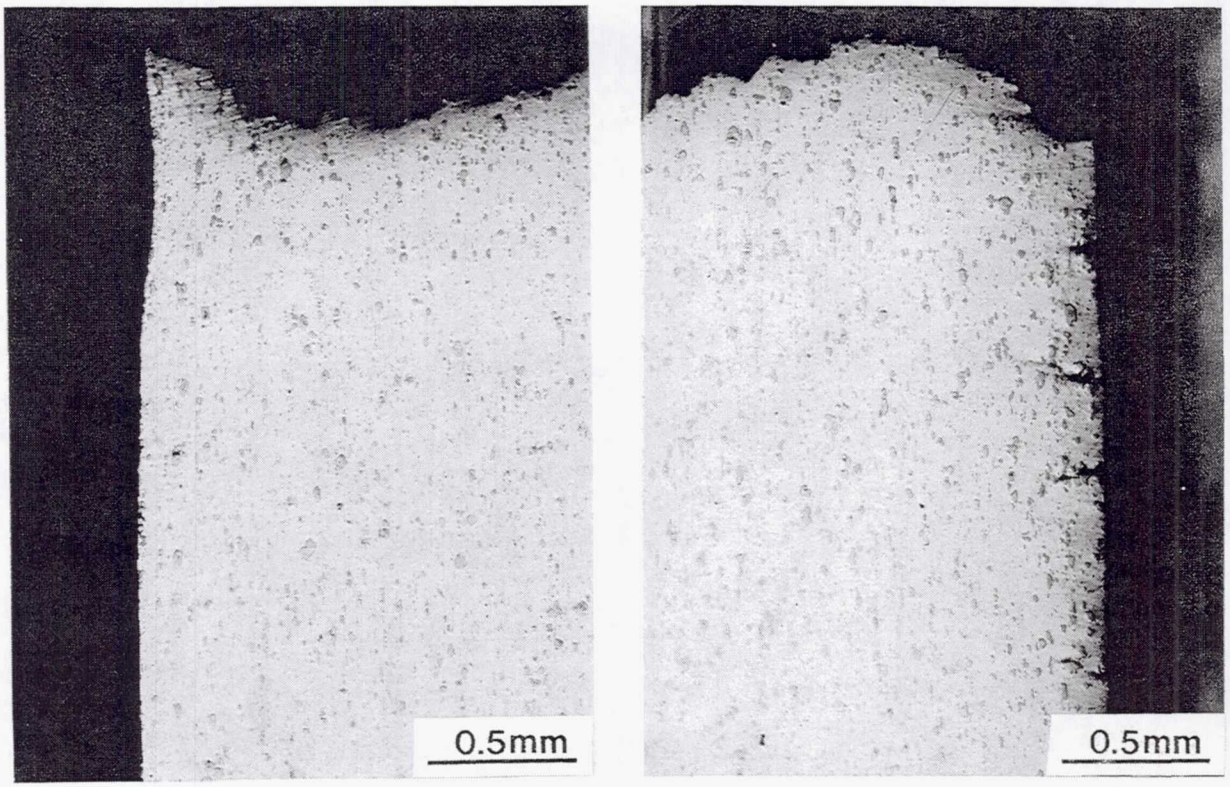


Figure 9. Effect of temperature on the tensile ductility of the extruded composites.



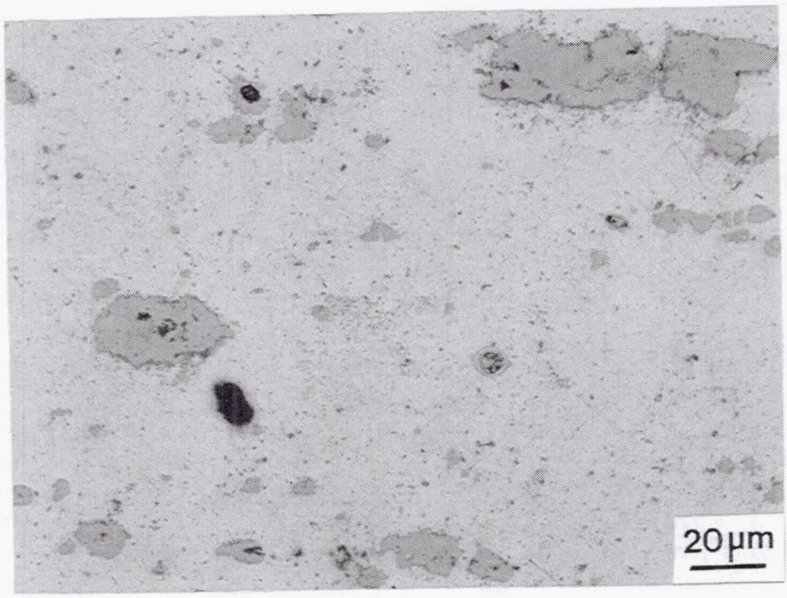
a b

Figure 10. Optical micrographs of polished longitudinal cross sections of fractured tensile specimens of the Cu - 7 vol.% ZrB_2 material: (a) 298K test and (b) 673K test.

evident in the 400°C specimen. Instead several surface cracks are seen in the latter (Fig. 10b). In both cases, large particles are seen (as large as 50 μm), fairly uniformly distributed throughout the section. Higher magnification micrographs of these particles are shown in Fig. 11a, b; it appears that these are individual particles rather than agglomerates (Fig. 11a) and further, frequently, they show a reaction zone that extends to a significant depth within the particles (Fig. 11b). From these observation, it appears unlikely that these large particles are agglomerates of ZrB_2. This microstructure was then examined in an SEM with an EDX attachment and the cross-section of one such particle as it appears in the SEM is shown in Fig. 12. Clearly, it is a single particle with a reaction zone in the middle of the cross-section forming a "necklace" around the core of the particle. Qualitative EDX analysis of the matrix and the various zones in the particle are provided in Fig 13a-d. Unfortunately, EDX is incapable of picking up a light element such as boron. The matrix is essentially Cu as it should be (Fig. 13a) and the outer layer of the particle is substantially Zr (Fig. 13b). This could be either elemental Zr, Zr-Cu solid solution, Zr-rich Zr-Cu intermetallic or ZrB_2. In the reacted region (region 2), a significant amount of Cu is present (Fig. 13c) suggesting either a Zr-Cu alloy or a ternary Zr-Cu boride. In the core of the particle, only Zr was present (Fig. 13d) and is likely unreacted elemental Zr.

Based on these observations, it is believed that the multiple cracks on the tensile specimen surface after testing at 400°C (Fig. 10b) may be a consequence of rapid oxidation of these Zr particles (see "The Metallurgy of Zirconium", edited by B. Lustman and F. Kerze, Jr., 1955, McGraw Hill Book Company, pp. 581-590) and the associated ductility loss with increasing temperature arising from this preferential oxidation. Alternately, the formation of Cu-Zr intermetallics in the unreacted Zr particles can lead to the presence of low melting phases which can also lead to ductility loss either directly or assisted by environment. The possibility of hydrogen

a



b

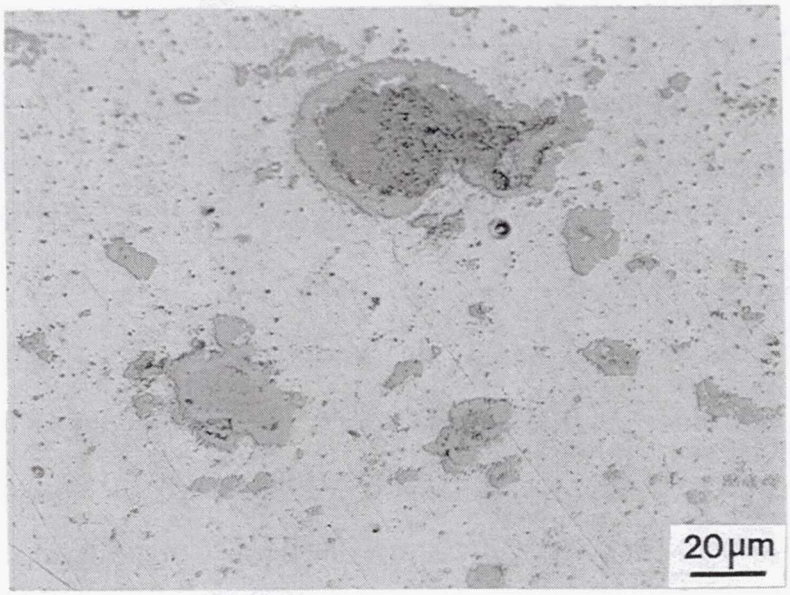


Figure 11. Higher magnification micrographs of the coarse particles in Figure 10: (a) 298K specimen and (b) 673K.

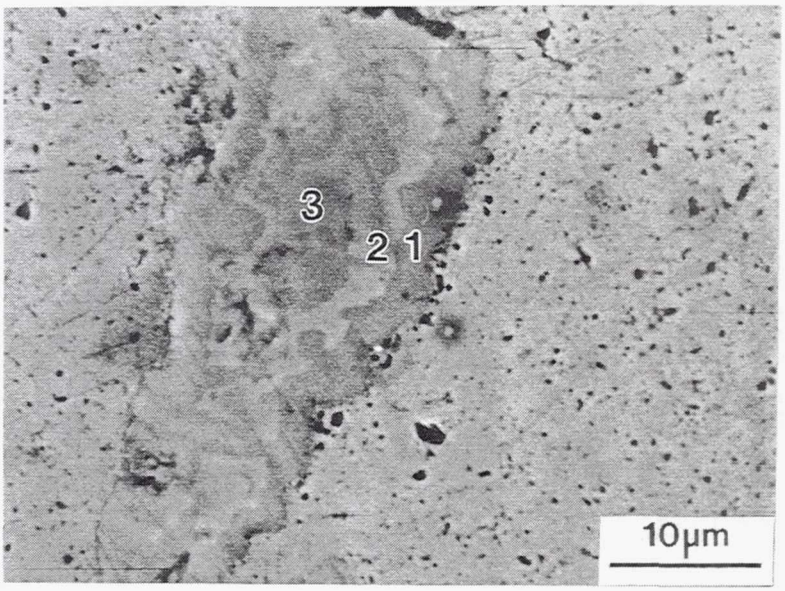


Figure 12. Scanning electron micrograph of cross-section of a coarse particle revealing the presence of a reacted zone in the interior suggesting that it is not a single (or an agglomerate) ZrB_2 particle.

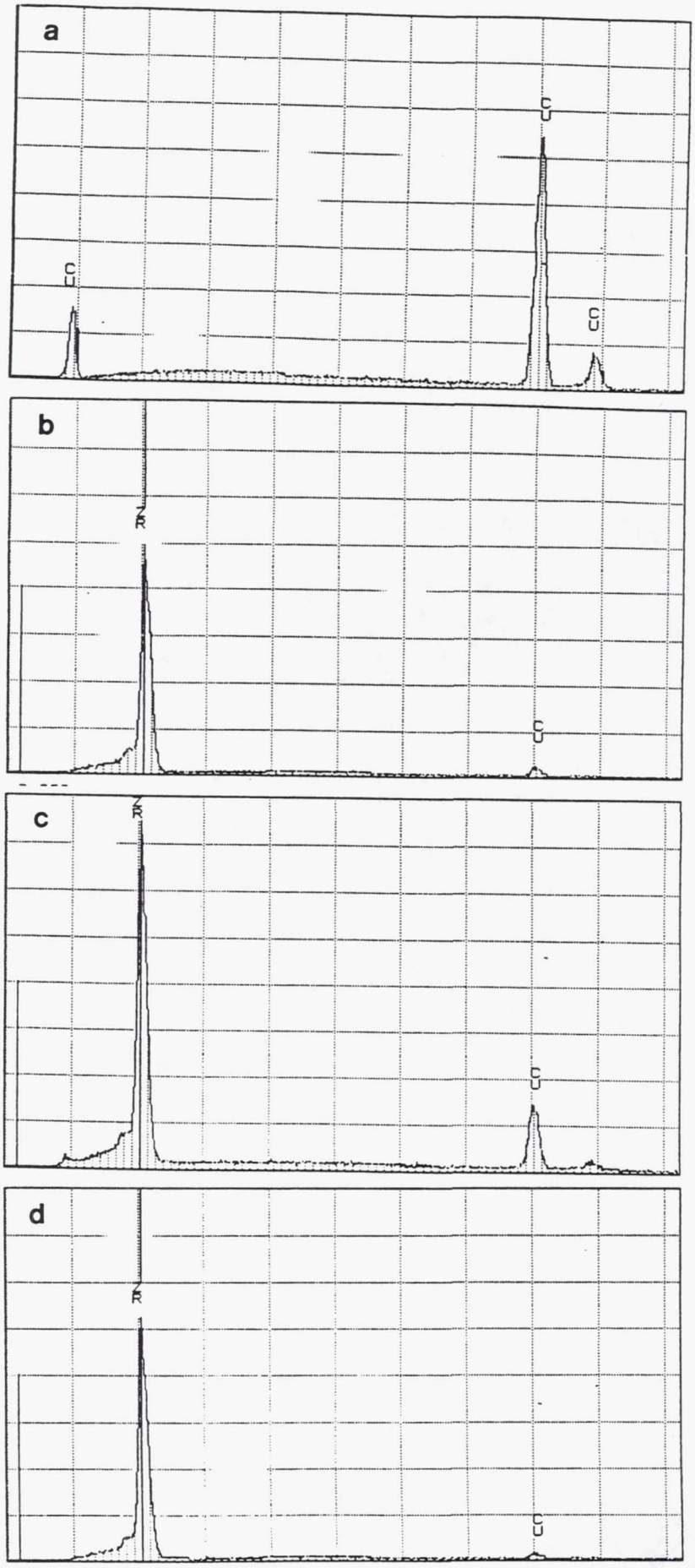
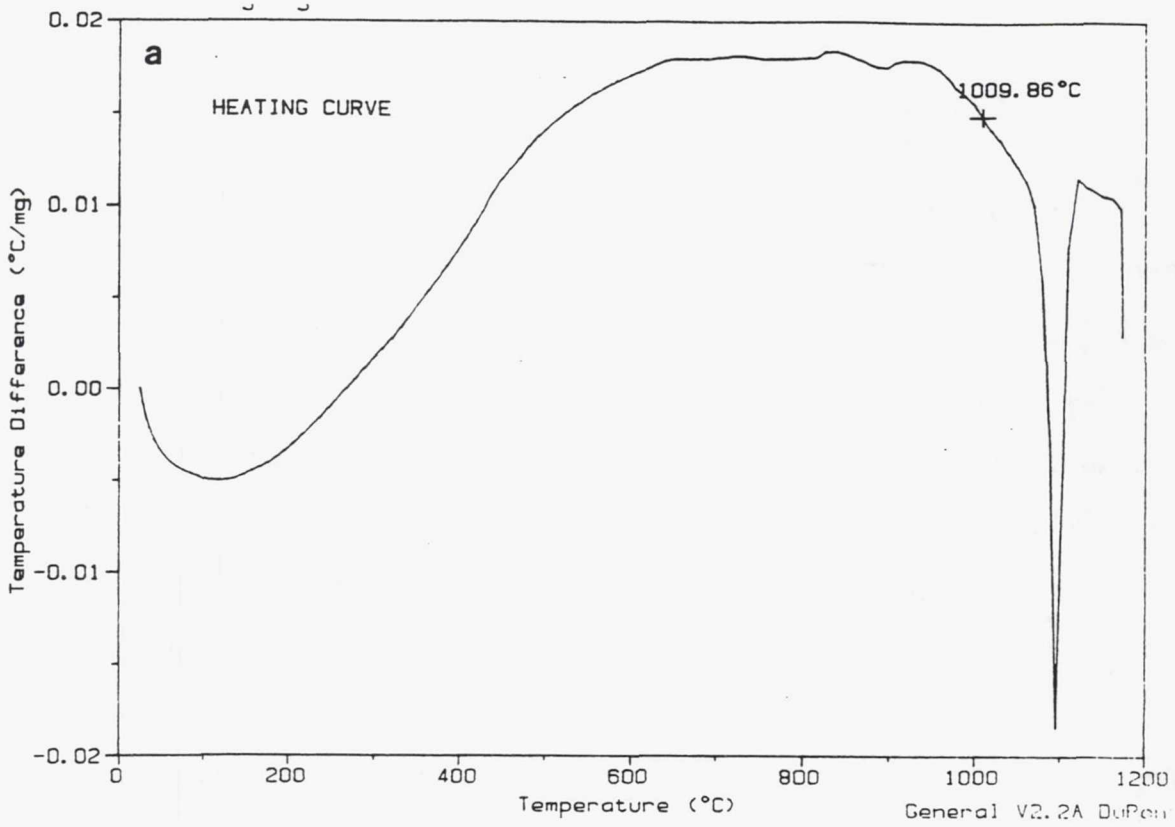


Figure 13. Qualitative EDX analysis of (a) matrix, (b) region 1, (c) region 2, and (d) region 3 in Figure 12.

attack of elemental zirconium must also be considered.

In an attempt to identify the possible presence of low-melting phases in this material, either stable (due to a low pseudobinary eutectic temperature between Cu and ZrB_2) or metastable (Cu-Zr intermetallics), a DTA scan was performed on the 15 vol.% ZrB_2 material upon heating from room temperature to 1200°C and upon cooling. The observed results are presented in Fig. 14a, b respectively. Upon heating, several minor endotherms are observed in the temperature range800°C to 925°C before complete melting occurs at ~1000°C. During cooling, solidification commences at about the melting point of Cu and is complete fairly soon thereafter, indicating a fairly narrow freezing range. Thus, if a pseudobinary eutectic exists, it is very close to the melting point of Cu. Below 1050°C, no further exotherms or endotherms are observed. This suggests that the minor endotherms during heating are a consequence of metastable incomplete reactions that are all completed upon melting and not reproduced on cooling.

Fracture surfaces of specimens tested at temperatures above 400°C were severely oxidized and could not be characterized. Representative micrographs of the fracture surfaces of specimens containing 7 vol.% and 15 vol.% ZrB_2, tested at room temperature, are shown in Fig. 15a, b. Ductile failure by microvoid coalescence is recognized interspersed with large areas of pull-out around the Zr particles. Fracture surfaces of specimens tested at 400°C however looked substantially oxidized and could not be characterized. Thus rapid oxidation at temperatures as low as 400°C is a serious problem in these alloys.



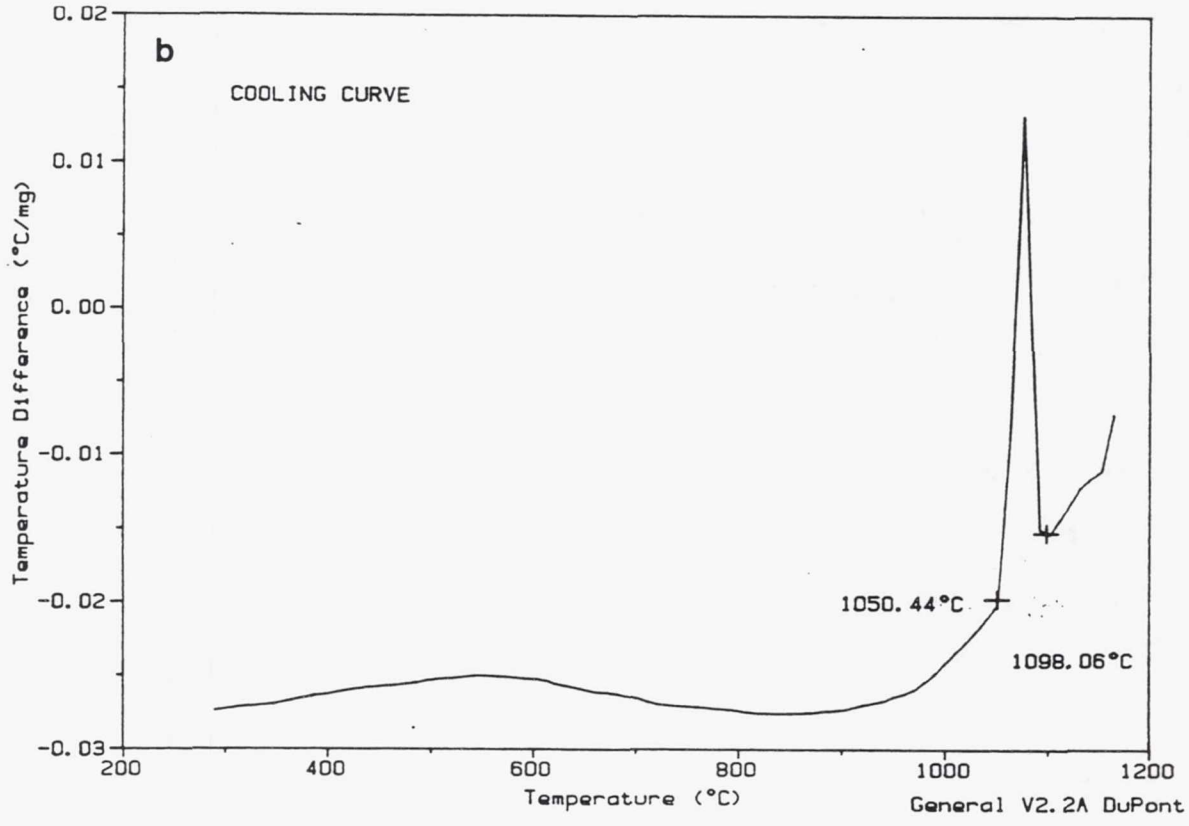
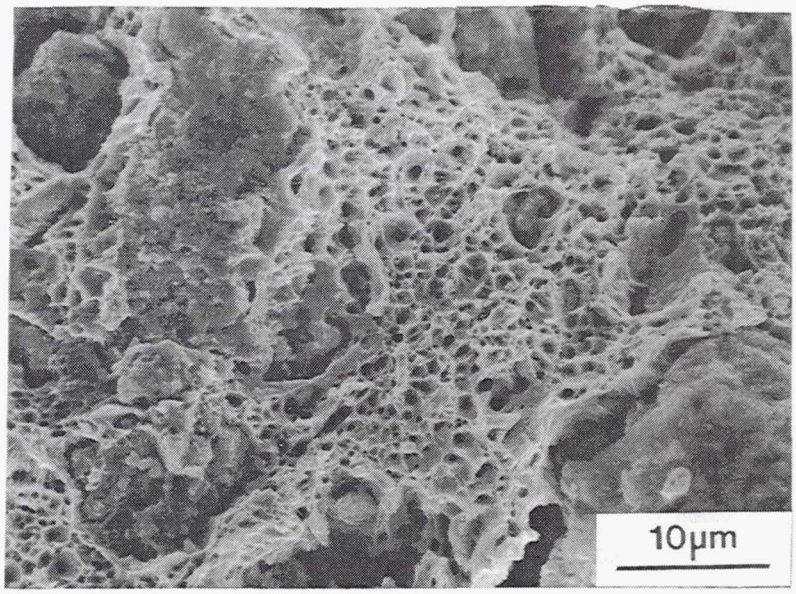


Figure 14. DTA scans of the Cu - 15 vol.% ZrB_2 material in the extruded condition (a) on heating, and (b) on cooling.

a



b

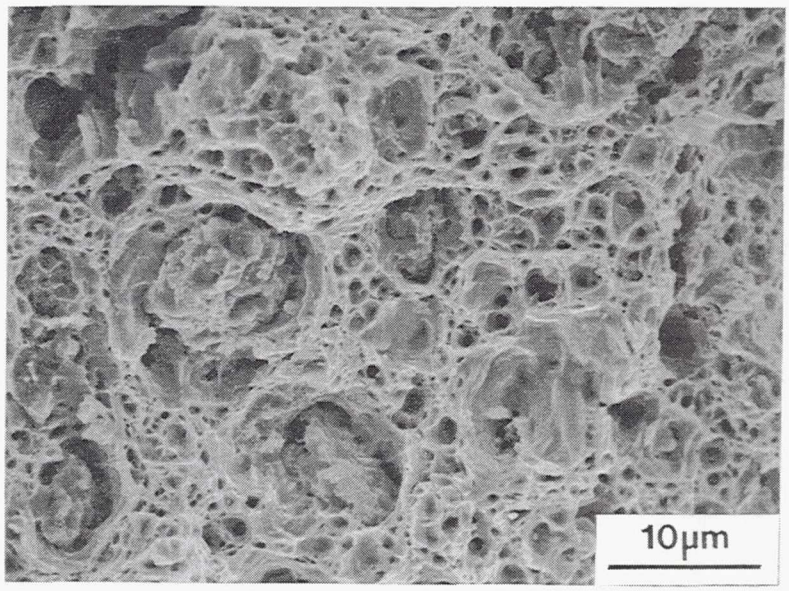


Figure 15. Representative fracture surface micrographs from specimens tested in tension at 298K: (a) 7 vol.% and (b) 15 vol.% ZrB_2 reinforcement.

VI. CONCLUSIONS

- Attempts were made to optimize the microstructure of XD™ Cu-ZrB_2 composites by manipulating the powder mixing parameters based on the argument that the cause for ZrB_2 particle agglomeration was inadequate mixing of the submicron boron powder.

- In this study it has been shown that the XD™ reaction does not go to completion in these materials, resulting in the presence of either elemental Zr or alloyed Zr-Cu particles that are extremely coarse (≤ 50 μm). This is not surprising because the volume fraction of ZrB_2 being considered is too low to generate enough heat from the exothermic reaction to make it self-sustaining, particularly in a high conductivity matrix such as Cu.

- It is believed that these coarse Zr particles are responsible for the low strengths (due to not enough submicron reinforcements being present) and the dramatic ductility loss with increasing temperatures. Further, it is believed that their presence, either in elemental Zr form or as ZrB_2 particles, will significantly decrease the oxidation resistance of these Cu alloys.

- Finally, caution must be exercised in optimizing mixing parameters because scale-up to larger batch sizes is not necessarily linear.

VII. RECOMMENDATIONS

Based on the observations in this study, it is recommended that if the direct synthesis route is to be used in future work in this area, a master alloy of Cu-ZrB_2 be initially prepared containing 60-80 vol.% of the reinforcement. The large heat of reaction from such a high volume fraction may permit the reaction to go to completion, thereby eliminating the presence of unreacted zirconium. This should then be blended with an appropriate amount of elemental Cu to obtain the desired dilution. This blend should then be high-energy milled to "knead" the ductile Cu into the concentrate. The efficiency of mixing will dictate the final distribution of the diboride in the material; this should be good based on the ability to obtain fine layered structures in the Cu powder where the individual layer thickness is in the same order of magnitude as the particle size. Subsequent extrusion using a high reduction ratio will further enhance the distribution of the reinforcement. Using a finer size distribution of Zr powders (e.g., ≤ 44 μm) would also help in improving the mixing response.

An alternative is to explore ingot metallurgy techniques, although it is anticipated that melt viscosity limitations may restrict the maximum loading to ~10 vol.% , although this argument remains to be proven for this specific system. In any event, it is believed that the presence of significant amounts of ZrB_2 (or elemental Zr) in Cu degrades the oxidation resistance of Cu and may lower its usefulness temperature range. This should be given serious consideration.

APPENDIX

HOT EXTRUSION DATA SHEET
(PFS-HotExtDS)

gineer's Name: Whittenberger/Kumar — Date Submitted: 92/09/21
g's ID: 1-15 b7 — Charge Number: YOG 2272 — Date Completed: 92/09/21

neral Type of Material: Cu-alloy

minal Composition: Cu + particulate ZrB2 (7 Vol. %)

pe of Billet: Casting
ze of Billet (inches) — Diameter: 3 — Length: 5.5

oposed Extrusion Conditions — Temperature (F): 1560 — Reduction Ratio: 24:1
Type of Die: Round
Punch Speed (inch/min): Max
Special Conditions:

fety Checks — Leak Test: — Date:
Heat Test (2h 1500F): — Date:

tual Extrusion Conditions — Date: 92/09/21 — Ext. ID: L-2904
Crew:
Temperature: 1560 — Reduction Ratio: 24:1
Type of Die Round: X Sh Bar: Other: Angle: 90
Special Conditions:

Valve Selection (X to specify) 1/8: 3.5: X 7/16: Valve Opening: Preset Punch Speed:

Side Ram: Pressure (psi): Max Tonnage:
Main Ram: Pressure (psi): Max Tonnage:
Comb Ram: X Pressure (psi): 2350 Max Tonnage: 640

Lubricant Container: Dylon Graphite Paper: X
Die: Formkote
Dummy Thickness: 1.5 Carbon Thickness: 2
Container Mat: Nu Die V Cont Temp (F): 600 Times Used: 542
Stem Material: Var 218 Stem ID: ? Times Used: 522

Time at Temperature (h): 3 Transfer Time (s): 4.8

st Test Analysis of Extrusion — Sucessful: X Unsucessful:
Comment:

Shooter: Butt left in Die: Sticker:
Break thru Pressure (ksi): 176.3 Punch Speed: 1.5 "/s
Running Pressure (ksi): 137.4 Time to Ext: 3.8 s
Condition of Extrusion: Extrusion in pieces

Length of Ext: 81 " Nominal Cross Section: 0.64 " dia
Condition of Die:

General Comments: Serrated load - time curve

HOT EXTRUSION DATA SHEET
(PFS-HotExtDS)

Engineer's Name: Whittenberger/Kumar — Date Submitted: 92/09/2
Eng's ID: 2-15 b7 — Charge Number: YOG 2272 — Date Completed: 92/09/2

General Type of Material: Cu-alloy

Nominal Composition: Cu + particulate ZrB2 (7 vol.%)

Type of Billet: Casting
Size of Billet (inches) — Diameter: 3 — Length: 5.5

Proposed Extrusion Conditions
Temperature (F): 1560 — Reduction Ratio: 24:1
Type of Die: Round
Punch Speed (inch/min): Max
Special Conditions:

Safety Checks
Leak Test: — Date:
Heat Test (2h 1500F): — Date:

Actual Extrusion Conditions
Date: 92/09/21 — Ext. ID: L-2905
Crew:
Temperature: 1560 — Reduction Ratio: 24:1
Type of Die Round: X Sh Bar: Other: Angle: 90
Special Conditions:

Valve Selection (X to specify) 1/8: 3.5: X 7/16: Preset Punch Speed:
Valve Opening:

Side Ram: Pressure (psi): Max Tonnage:
Main Ram: Pressure (psi): Max Tonnage:
Comb Ram: X Pressure (psi): 2350 Max Tonnage: 640

Lubricant Container: Dylon Graphite Paper: X
Die: Formkote
Dummy Thickness: 1.5 Carbon Thickness: 2
Container Mat: Nu Die V Cont Temp (F): 600 Times Used: 543
Stem Material: Var 218 Stem ID: ? Times Used: 523

Time at Temperature (h): 3.1 Transfer Time (s): 6

Post Test Analysis of Extrusion
Sucessful: X Unsucessful:
Comment:

Shooter: Butt left in Die: Sticker:
Break thru Pressure (ksi): 176.3 Punch Speed: 1.4 "/
Running Pressure (ksi): 111.6 Time to Ext:
Condition of Extrusion: Extrusion in pieces

Length of Ext: 80 " Nominal Cross Section: 0.63 " di
Condition of Die:

General Comments: Serrated lod - time curve

HOT EXTRUSION DATA SHEET
(PFS-HotExtDS)

gineer's Name: Whittenberger/Kumar — Date Submitted: 92/09/21
g's ID: 1-15 abc — Charge Number: YOG 2272 — Date Completed: 92/09/21

neral Type of Material: Cu-alloy

minal Composition: Cu + particulate ZrB2 (15 vol.%)

pe of Billet: Casting
ze of Billet (inches) — Diameter: 3 — Length: 5.5

oposed Extrusion Conditions
Temperature (F): 1560 — Reduction Ratio: 24:1
Type of Die: Round
Punch Speed (inch/min): Max
Special Conditions:

fety Checks
Leak Test: — Date:
Heat Test (2h 1500F): — Date:

tual Extrusion Conditions
Date: 92/09/21 — Ext. ID: L-2899
Crew:
Temperature: 1560 — Reduction Ratio: 24:1
Type of Die Round: X Sh Bar: Other: Angle: 90
Special Conditions:

Valve Selection (X to specify) 1/8: 7/16: Preset Punch Speed:
3.5: X Valve Opening:

Side Ram: Pressure (psi): Max Tonnage:
Main Ram: Pressure (psi): Max Tonnage:
Comb Ram: X Pressure (psi): 2350 Max Tonnage: 640

Lubricant Container: Dylon — Graphite Paper: X
Die: Formkote
Dummy Thickness: 1.5 — Carbon Thickness: 2
Container Mat: Nu Die V Cont Temp (F): 600 Times Used: 537
Stem Material: Var 218 — Stem ID: ? — Times Used: 517

Time at Temperature (h): 2.4 — Transfer Time (s): 11

st Test Analysis of Extrusion
Sucessful: X Unsucessful:
Comment:

Shooter: Butt left in Die: Sticker:
Break thru Pressure (ksi): 181.9 — Punch Speed: 1.1 "/s
Running Pressure (ksi): 133.4 — Time to Ext: 4.9 s
Condition of Extrusion:

Length of Ext: 80 " — Nominal Cross Section: 0.63 " dia
Condition of Die:

General Comments:

HOT EXTRUSION DATA SHEET
(PFS-HotExtDS)

Engineer's Name: Whittenberger/Kumar — Date Submitted: 92/09/
Eng's ID: 2-15 abc — Charge Number: YOG 2272 — Date Completed: 92/09/

General Type of Material: Cu-alloy

Nominal Composition: Cu + particulate ZrB2 (15 Vol.%)

Type of Billet: Casting
Size of Billet (inches) — Diameter: 3 — Length: 5.5

Proposed Extrusion Conditions
Temperature (F): 1560 — Reduction Ratio: 24:1
Type of Die: Round
Punch Speed (inch/min): Max
Special Conditions:

Safety Checks
Leak Test: — Date:
Heat Test (2h 1500F): — Date:

Actual Extrusion Conditions
Date: 92/09/21 — Ext. ID: L-2900
Crew:
Temperature: 1560 — Reduction Ratio: 24:1
Type of Die Round: X Sh Bar: Other: Angle: 90
Special Conditions:

Valve Selection (X to specify) 1/8: 3.5: X 7/16: Preset Punch Speed:
Valve Opening:

Side Ram: Pressure (psi): Max Tonnage:
Main Ram: Pressure (psi): Max Tonnage:
Comb Ram: X Pressure (psi): 2350 Max Tonnage: 640

Lubricant Container: Dylon — Graphite Paper: X
Die: Formkote
Dummy Thickness: 1.5 — Carbon Thickness: 2
Container Mat: Nu Die V Cont Temp (F): 600 Times Used: 538
Stem Material: Var 218 — Stem ID: ? — Times Used: 518

Time at Temperature (h): 2.3 — Transfer Time (s): 5

Post Test Analysis of Extrusion
Sucessful: X Unsucessful:
Comment:

Shooter: Butt left in Die: Sticker:
Break thru Pressure (ksi): 180.4 — Punch Speed: 1.3 "/
Running Pressure (ksi): 133.4 — Time to Ext: 4.1 s
Condition of Extrusion: Extrusion in pieces

Length of Ext: 87 — Nominal Cross Section: 0.64 " di
Condition of Die:

General Comments:

HOT EXTRUSION DATA SHEET
(PFS-HotExtDS)

gineer's Name: Whittenberger/Kumar Date Submitted: 92/09/21
g's ID: 3-15 abc Charge Number: YOG 2272 Date Completed: 92/09/21

neral Type of Material: Cu-alloy

minal Composition: Cu + particulate ZrB2 (15 vol.%)

pe of Billet: Casting
ze of Billet (inches) Diameter: 3 Length: 5.5

oposed Extrusion Conditions
Temperature (F): 1560 Reduction Ratio: 24:1
Type of Die: Round
Punch Speed (inch/min): Max
Special Conditions:

fety Checks
Leak Test: Date:
Heat Test (2h 1500F): Date:

tual Extrusion Conditions
Date: 92/09/21 Ext. ID: L-2901
Crew:
Temperature: 1560 Reduction Ratio: 24:1
Type of Die Round: X Sh Bar: Other: Angle: 90
Special Conditions:

Valve Selection (X to specify) 1/8: 7/16: Preset Punch Speed:
3.5: X Valve Opening:

Side Ram: Pressure (psi): Max Tonnage:
Main Ram: Pressure (psi): Max Tonnage:
Comb Ram: X Pressure (psi): 2350 Max Tonnage: 640

Lubricant Container: Dylon Graphite Paper: X
Die: Formkote
Dummy Thickness: 1.5 Carbon Thickness: 2
Container Mat: Nu Die V Cont Temp (F): 600 Times Used: 539
Stem Material: Var 218 Stem ID: ? Times Used: 519

Time at Temperature (h): 2.5 Transfer Time (s): 5.6

t Test Analysis f Extrusion
Sucessful: X Unsucessful:
Comment:

Shooter: Butt left in Die: Sticker:
Break thru Pressure (ksi): 176.3 Punch Speed: 1.3 "/s
Running Pressure (ksi): 101.6 Time to Ext: 4.3 s
Condition of Extrusion:

Length of Ext: 80.3 " Nominal Cross Section: 0.64 " dia
Condition of Die:

General Comments:

HOT EXTRUSION DATA SHEET
(PFS-HotExtDS)

Engineer's Name: Whittenberger/Kumar — Date Submitted: 92/09/2
Eng's ID: 4-15 abc — Charge Number: YOG 2272 — Date Completed: 92/09/2

General Type of Material: Cu-alloy

Nominal Composition: Cu + particulate ZrB2 (15 vol.%)

Type of Billet: Casting
Size of Billet (inches) Diameter: 3 Length: 5.5

Proposed Extrusion Conditions
Temperature (F): 1560 Reduction Ratio: 24:1
Type of Die: Round
Punch Speed (inch/min): Max
Special Conditions:

Safety Checks
Leak Test: Date:
Heat Test (2h 1500F): Date:

Actual Extrusion Conditions
Date: 92/09/21 Ext. ID: L-2902
Crew:
Temperature: 1560 Reduction Ratio: 24:1
Type of Die Round: X Sh Bar: Other: Angle: 90
Special Conditions:

Valve Selection (X to specify) 1/8: 7/16: Preset Punch Speed:
3.5: X Valve Opening:

Side Ram: Pressure (psi): Max Tonnage:
Main Ram: Pressure (psi): Max Tonnage:
Comb Ram: X Pressure (psi): 2350 Max Tonnage: 640

Lubricant Container: Dylon Graphite Paper: X
Die: Formkote
Dummy Thickness: 1.5 Carbon Thickness: 2
Container Mat: Nu Die V Cont Temp (F): 600 Times Used: 540
Stem Material: Var 218 Stem ID: ? Times Used: 520

Time at Temperature (h): 2.6 Transfer Time (s): 5.5

Post Test Analysis of Extrusion
Sucessful: X Unsucessful:
Comment:

Shooter: Butt left in Die: Sticker:
Break thru Pressure (ksi): 181.9 Punch Speed: 1.2 "/
Running Pressure (ksi): 133.4 Time to Ext: 4.7 s
Condition of Extrusion: Extrusion in pieces

Length of Ext: 81 Nominal Cross Section: 0.63 " di
Condition of Die:

General Comments: Serrations in load - time curve

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13. ABSTRACT ***(Maximum 200 words)***

In a previous effort sponsored by the NASA Lewis Research Center, the XD™ process was used to produce ZrB_2 particulate reinforcements in Cu and the resulting extruded material was microstructurally characterized and evaluated in tension over a range of temperatures. A problem that was encountered in that study was microstructural inhomogeneity resulting from the frequent presence of "ZrB_2 agglomerates" that were several microns in size. The presence of these agglomerates was attributed to improper mixing of powders in the green compact used in the XD™ process and specifically, to elemental boron powder segregation. In this program, several milling parameters were examined in an effort to optimize this processing step; two levels of ZrB_2 reinforcements were considered (7 vol.% and 15 vol.%). Microstructures of the reacted powder mass were examined to verify the absence of these agglomerates. Larger batches of powder were then mixed, reacted, machined to size, canned and extruded. The microstructure and tensile properties of these extrusions were examined, and the measured properties were correlated with the observed microstructure. Large unreacted or partially reacted Zr particles were present that affected the mechanical properties deleteriously and their presence is attributed to insufficient heat of reaction during XD™ synthesis. Alternate processing routes are recommended.

14. SUBJECT TERMS

Copper; Zirconium; Boron; Copper alloy; Dispersion strengthened; Tensile strength

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