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13. ABSTRACT (Maximum 200 words)

Transformation superplasticity - defined as the capability of allotropic materials to deform rapidly and without fracture upon thermal cycling around their phase transformation temperature - has been studied in a range of monolithic and composite materials systems: metals (Fe, Ti and Zr), metal matrix composites (Ti6Al4V-TiC, Ti6Al4V-TiB and Fe-TiC), intermetallic matrix composites (NiAl-ZrO2), ceramics (Bi2O3) and ceramic matrix composites (zirconia-based system). Often, samples were fabricated in house by powder processes and in all cases their microstructure was characterized before and after deformation. Tensile experiments demonstrated that samples deform more rapidly and to higher fracture strains when thermally cycled around their phase transformation than when held at a constant equivalent temperature. Furthermore, theoretical modeling was performed using both analytical closed-form solution methods and finite-element numerical methods, and good agreement with experimental data was obtained. Major transformation superplasticity mile-stones include: first complete study of zirconium, first demonstration in intermetallic systems (titanium aluminide and nickel aluminide), first demonstration in ceramic systems (bismuth oxide and zirconia), first numerical model (finite-element), new continuum model (at high stresses), first demonstration of whisker alignment (in Ti-6Al-4V/TiB), first use of hydrogen (in Ti). Also, our collaboration with industry has resulted in a completed Phase I SBIR project as well as a subsequent Phase II project initiated in 2000 with NSF sponsorship, an important step towards commercialization of transformation superplasticity.

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Transformation Superplasticity of Intermetallic and Ceramic Matrix Composites

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Abstract

Transformation superplasticity - defined as the capability of allotropic materials to deform rapidly and without fracture upon thermal cycling between their two phases - has been studied in a series of monolithic and composite materials systems: metals (Fe, Ti and Zr), metal matrix composites (Ti6Al4V-TiC, Ti6Al4V-TiB and Fe-TiC), intermetallic matrix composites (NiAl-ZrO_2), ceramics (Bi_2O_3) and ceramic matrix composites (zirconia-based system). Often, samples were fabricated in house by powder processes and in all cases their microstructure was characterized before and after deformation. Tensile experiments demonstrated that samples deform more rapidly and to higher fracture strains when thermally cycled around their phase transformation than when held at a constant equivalent temperature. Furthermore, theoretical modeling was performed using both analytical closed-form solution methods and finite-element numerical methods, and good agreement with experimental data was obtained. Major transformation superplasticity milestones include: first complete study of zirconium, first demonstration in intermetallic systems (titanium aluminide and nickel aluminide), first demonstration in ceramic systems (bismuth oxide and zirconia), first numerical model (finite-element), new continuum model (at high stresses), first demonstration of whisker alignment (in Ti-6Al-4V/TiB), first use of hydrogen (in Ti). Also, our collaboration with industry has resulted in a completed Phase I SBIR project as well as a subsequent Phase II project initiated in 2000 with NSF sponsorship, an important step towards commercialization of transformation superplasticity.

Statement of Problem Studied

Unlike the well-known and much-studied microstructural superplasticity which relies on grain-boundary sliding in very fine-grain materials, transformation superplasticity relies on the formation of internal stresses upon thermal cycling around a phase transformation temperature, and can thus be used in allotropic materials with arbitrary grain size. While transformation superplasticity has been studied sporadically in the past in metals and alloys, it is unexplored in advanced materials such as intermetallics, ceramics and their composites. The pay-off of using transformation superplasticity for these materials is high, because their hardness and brittleness precludes traditional forming and their grain-size is often too large for microstructural superplasticity. The goal of the present study is to demonstrate transformation superplasticity in a variety of advanced materials and also advance our theoretical understanding of this little-studied deformation mechanism.

Summary of Most Important Results

1. Metals and metal matrix composites

Because they are easier to fabricate and test, metals and metal matrix composites were used as model materials for transformation superplasticity of intermetallic and ceramic composites.

Previously ongoing experiments on biaxial superplastic forming of titanium and Ti-based metal matrix composites were completed by Miojin and the results were found to agree with existing superplastic models. This was the first demonstration that transformation superplasticity can be used in complex deformation geometries and stress states and it validated transformation superplasticity for the industrial use in forming complex objects.

Zwigl focused on three metallic systems: zirconium, titanium and iron, as well as composites of the latter two metals. For zirconium, he carried out the first comprehensive study on this metal and demonstrated for the first time very high strains to fracture. In titanium composites, he showed for the first time that alloyed matrices (Ti-6Al-4V) exhibited transformation superplasticity comparable to previous results from Bedell on unalloyed titanium composites. He systematically studied the thermal cycling frequency and amplitude, as well as demonstrated remarkable sample elongations of about 500%. In iron composites, he generated basic data on superplastic strain per cycle for two different volume fractions carbide reinforcement (10% and 20%) as well as control samples without TiC. Finally, Zwigl made significant progress on the general modeling of transformation superplasticity, using both analytical and finite element formulations. A new solution for valid for all applied stresses was developed, representing a significant improvement as compared to the existing model valid only at small stresses.

Schuh investigated metal matrix composites based on the alloy Ti6Al4V. An important discovery was the alignment of short TiB fibers in the Ti6Al4V matrix after deformation, which is known in materials deforming by fine-grain superplasticity but had never been observed for transformation superplasticity. He also successfully modeled this phenomenon using a continuum mechanics approach. Also, Schuh reported for the first time mechanical properties of composites after deformation by transformation superplasticity, a necessary step for the technological use of this technique.

In anticipation of a renewal contract for 1999-2002 for which a proposal had been submitted to Dr. W. Simmons at ARO in 1998, transformation superplasticity induced by hydrogen cycling (rather than temperature cycling) was explored by Zwigl in titanium and Ti-6Al-4V. This is a radically new idea and research progressed enough to deposit a patent. However, following the retirement of Dr. Simmons, ARO did not renew the present contract, so further research was stopped on hydrogen cycling. A recent award from NSF in the summer of 2000 will however allow restart of this research, so preliminary results from the present ARO-sponsored project will not be wasted. Also, Frary and Schuh performed a preliminary study of cyclical hydrogen alloying and dealloying of titanium without applied stress. They observed a small amount of ratchetting (length change due to cycling), similar to the ratchetting observed upon thermal cycling of allotropic materials. This is the first observation of "chemical ratchetting" which is of significance also for hydrogen-storing materials subjected to multiple loading and unloading with hydrogen.

2. Intermetallics and intermetallic matrix composites

Zwigl fabricated NiAl-ZrO_2 composites containing 10 and 20% unstabilized zirconia particulates. He started by heat-treating different grades of zirconia to manipulate the transformation temperature, such that it was in the optimal temperature creep range for

NiAl. The composites were found to exhibit a phase transformation by thermal analysis at the same temperature as the zirconia, indicating that internal stresses did not affect this property. Finally, tensile samples were tested under temperature cycling conditions and shown to exhibit faster deformation than under isothermal conditions: this is the first experimental demonstration of transformation superplasticity in an intermetallic matrix composite. A numerical model using the finite-element code ABAQUS as developed and successfully compared to experiments. This is also the first-time that finite-element methods have been used to study TSP.

Schuh studied super-$\alpha 2$ titanium aluminide and demonstrated tensile elongation in excess of 500% upon cycling between the ordered and disordered phases. This is the first demonstration of transformation superplasticity in an intermetallic. He systematically studied the effect of stress, cycling frequency and cycling amplitude and also performed a comparative creep study under isothermal conditions. A complete model of the phenomenon was developed, which included issues of creep relaxation, broad transformation range and transformation hysteresis. Schuh also studied a two-phase α-γ TiAl-base intermetallic where no transformation occurs but internal stresses can be produced by mismatch in thermal expansion between the phases. No superplastic effect was observed, a technologically-important result which also lends credence to the assumption made in our TSP models that thermal mismatch can be neglected.

3. Ceramics and ceramic matrix composites

Whitney fabricated by hot-pressing composites of stabilized, fine-grained zirconia containing unstabilized zirconia particles. The composites were tested by dilatometry and thermal analysis to determine the transformation temperature of the zirconia particulates, which was found to be lower than expected because of large internal constraints. Whitney demonstrated TSP in these composite as enhanced deformation was obtained in compression when the particles transformed, but these results were limited by cracking of the matrix. After Whitney's graduation, Balch continued the study of these ceramic composites and fabricated a new batch of copper-doped matrix, which was expected to increase the creep rate and thus inhibit cracking. Non-renewal of the present project put an end to this promising line of study before final results could be obtained (Balch had to change his Ph.D. thesis project which is sponsored by another source).

Grabowski studied the oxide ceramic Bi_2O_3, a low-temperature analog to zirconia with a phase transformation temperature of about 720 °C. He determined the optimal processing conditions for sintering of dense specimens and carried tensile experiments at elevated temperature, both under isothermal conditions (as control) and under thermal cycling conditions, where enhanced deformation rate were observed. A major accomplishment was the demonstration, for the first time, of transformation superplasticity in a coarse-grain ceramic, as evidenced by large tensile strains (up to 28%) and a linear relationship between applied stress and average strain-rate. Further x-ray investigations were performed to determine exactly which allotropes were responsible for deformation.

4. Technology Transfer

Dynamet Technology Inc. (Burlington, MA) is a small company specializing in the fabrication of titanium composites reinforced with TiC particles or TiB whiskers. They have shown for many years great interest in the technology of transformation superplasticity for forming complex objects from their very hard composites. They submitted together with the PI a SBIR proposal on transformation superplasticity to the National Science Foundation which was funded. The follow-up Phase II was also funded and started in late 1999, with the aim of developing sporting good equipment out of composites shaped by transformation superplasticity.

List of Publications

1. Journal Articles

1. D.C. Dunand, S. Myojin
"Biaxial Deformation of Ti-6Al-4V and Ti-6Al-4V/TiC Composites by Transformation-Mismatch Superplasticity"
Materials Science and Engineering A, **230**, 25-32 (1997).

2. P. Zwigl, D.C. Dunand
"A Non-Linear Model for Internal Stress Superplasticity"
Acta Materialia, **45**, 12, 5285-5294 (1997).

3. P. Zwigl, D.C. Dunand
"Transformation Superplasticity of Iron and Fe/TiC Metal Matrix Composites"
Metallurgical and Materials Transactions, **29A**, 2, 565-575 (1998).

4. P. Zwigl, D.C. Dunand
"Transformation Superplasticity of Zirconium"
Metallurgical and Materials Transactions, **29A**, 10, 2571-2582 (1998).

5. C. Schuh, D.C. Dunand
"Transformation Superplasticity of Super $\alpha 2$ Titanium Aluminide"
Acta Materialia, **46**, 16, 5663-5675 (1998).

6. P. Zwigl, D.C. Dunand
"A Numerical Model of Transformation Superplasticity for Iron"
Materials Science and Engineering A, **262**, 166-172 (1999).

7. C. Schuh, D.C. Dunand, A. Wanner, H. Clemens
"Thermal-Cycling Creep of γ-TiAl-Based Alloys"
Intermetallics, **8**, 4, 339-343 (2000).

8. C. Schuh, D.C. Dunand
"Whisker Alignment in Ti-6Al-4V/TiB Composites during Deformation by Transformation Superplasticity "
International Journal of Plasticity, in print.

9. M. Frary, C. Schuh, D.C. Dunand
"Strain Ratchetting of Titanium upon Reversible Alloying with Hydrogen"
Philosophical Magazine, in print.

10. D.C. Dunand, J.L. Grabowski
"Tensile Transformation-Mismatch Plasticity of Bi_2O_3"
Journal of the American Ceramic Society, in print.

11. J.L. Grabowski, D.C. Dunand
"Tensile Creep Properties of δ–Bi_2O_3"
Scripta Materialia, in print.

12. P. Zwigl, D.C. Dunand,
Transformation-Mismatch Plasticity of $NiAl/ZrO_2$ Composites - Experiments and Continuum Modeling
Materials Science and Engineering A, in print.

2. Conference Articles

1. C.B. Bedell, P. Zwigl, D.C. Dunand
"Transformation-Mismatch Superplasticity in Pure Titanium and a Titanium Matrix Composite"
Superplasticity and Superplastic Forming
(edited by A.K. Ghosh, and T.R. Bieler)
TMS, Warrendale, 125-133 (1995).

2. P. Zwigl, D.C. Dunand
"Transformation Superplasticity of Iron: Modeling and Experimental Evidence"
International Symposium on Superplasticity in Materials, International Conference on Thermomechanical Processing of Steels and Other Materials
(edited by T. Chandra and T. Sakai)
TMS Warrendale, 1831-1838 (1997).

3. D.C. Dunand
"Transformation Superplasticity in Metals, Alloys and Composites" (Invited Paper)
International Symposium on Superplasticity in Materials, International Conference on Thermomechanical Processing of Steels and Other Materials
(edited by T. Chandra and T. Sakai)
TMS Warrendale, 1821-1830 (1997).

4. P. Zwigl, D.C. Dunand
"Finite-Element Modeling of Transformation Superplasticity in Composites with Allotropic Particles"
German-Austrian ABAQUS User Conference
Institut fuer Fertigkeitslehre, Innsbruck University (Austria) 75-88 (1997).

5. P. Zwigl, D.C. Dunand
"Numerical Modeling of Transformation Superplasticity for an Elastic, Ideally-Plastic Material"
Superplasticity and Superplastic Forming 1998
(edited by A.K. Ghosh and T.R. Bieler)
TMS Warrendale, 239-246 (1998).

6. P. Zwigl, D.C. Dunand
"Transformation Mismatch Plasticity in NiAl/ZrO_2 Intermetallic Matrix Composites"
Superplasticity and Superplastic Forming 1998 (Supplemental Volume)
(edited by A.K. Ghosh and T.R. Bieler)
TMS Warrendale, 40-47 (1998).

7. C. Schuh, W. Zimmer, D.C. Dunand
"Microstructure and Properties of Titanium and Ti-6Al-4V with and without TiC_p Reinforcement Deformed by Transformation Superplasticity"
Creep Behavior of Advanced Materials for the 21st Century
(edited by R.S. Mishra, A.K. Mukherjee and K.L. Murty)
TMS Warrendale, 61-70 (1999)

List of Personnel and Advanced Degrees

1. Personnel

PI
Prof. David Dunand (MIT and NU)

Ph.D. Students
Dorian Balch (NU)
Christopher Schuh (NU)
Peter Zwigl (Ph.D. at MIT and post-doc at NU)

M.S. Students
Jeffrey Grabowski (NU)
Michael Whitney (MIT)

2. Advanced Degrees Granted

Michael Whitney ,
"Transformation Superplasticity of Ceramic Matrix Composites",
Massachusetts Institute of Technology, M.S., June 1997.

Peter Zwigl,
"Transformation Superplasticity of Metals and Metal Matrix Composites",
Massachusetts Institute of Technology, Ph.D., February 1998.

Jeffrey L. Grabowski,
"Transformation Superplasticity of Bismuth Oxide"
Northwestern University, M.S., June 1998.

Report of Inventions

D.C. Dunand, P. Zwigl
"Chemically Induced Superplastic Deformation"
US Patent No. 6,042,661, March 28, 2000.